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A tong-like fluorescence sensor for metal ions: perfect conformational switch of hinge sugar by pyrene stacking†

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Carbohydrates are among the potential materials for molecular devices, since they are abundant natural resources. However, their rigidity has restricted their use for movable devices. Hinge sugars, 2,4-diamino-2,4-dideoxy-xylopyranosides, shed light on the use of carbohydrates as movable components, as demonstrated by the motion by which all four equatorial substituents can change to an axial orientation in synchronization with a chelation-driven $^4C_1$–$^1C_4$ ring flip. In this study, we synthesized a tong-like metal ion sensor, 1,3-di-*O*-pyrenylmethylated hinge sugar (**1**), and its model compound, methyl 2,4-di-*O*-pyrenecarbonyl-xylopyranoside (**2**), to extend the abilities of hinge sugars as molecular components. From observations of the solvent-dependent conformational and fluorescent behavior of **2**, we found that the pyrene stacking assists the $^1C_4$ formation of xylopyranoside by 1.7 kcal mol^{-1}. We also found that compound **1** produced excimer fluorescence by chelation to Pt^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+} or Mn^{2+}, and unexpectedly by addition of acids. ^{1}H NMR measurements ascribed this behavior to the $^4C_1$–$^1C_4$ ring flip of hinge sugar in response to chelation or protonation at N2, and revealed rapid and perfect $^1C_4$ formation in the case of Zn^{2+}. These findings will extend the scope of hinge sugars as movable components.

Introduction

Carbohydrates are abundant natural resources and therefore they have been used as raw materials for drugs, functional polymers, and molecular devices.[1] The material properties one may expect for carbohydrates would be their hydrophilicity and rigidity. In supramolecular chemistry, these properties of carbohydrates are exploited in the frameworks of molecular devices, as illustrated by cyclodextrins,[2] in which the partial hydrophobicity of their hollows also plays a role in encapsulating small molecules. On the other hand, the functions of a number of molecular devices rely on the conformational changes of their movable components.[3] The motions of these components include spatial transitions of non-covalent bonds, isomerizations of double bonds, and free-rotations of single bonds. Although single bonds are the simplest components to be assembled into a device, a restriction in their rotation is often required for the precise function of the device. This rotational restriction is attainable by ring flips of cyclic compounds. If a carbohydrate undergoes ring flips in a controlled fashion, it is an attractive material for molecular devices together with its abundance, chiral properties, and biocompatibility. Thus, the development of carbohydrates as movable components is an important issue to be addressed.

Cyclohexanes have been employed as the movable components of pyrene-based excimer fluorescence sensors (Fig. 1).[4] These cyclohexane rings have two equatorial and two axial substituents, and the orientations of these substituents are alternated by a ring flip. The diaxial repulsion in each conformer is compensated by anchoring a pair of substituents in the equatorial orientation. These cyclohexane-based sensors can chelate metal ions by rearranging the diequatorial ligand groups into diaxial orientation. In concert with this chelation, the diaxial substituents bearing the stacked pyrene groups are rearranged into diequatorial orientation, which unstacks the pyrene groups and thus extinguishes excimer fluorescence. This whole motion can be regarded as a clothespin-like motion, which is easier for cyclohexanes to trace than a tong-like motion that requires highly constrained four axial substituents in its closed form.

Pyranose is considered a better ring system to accommodate axial substituents than cyclohexanes, because anomeric effects[5] favour the axial orientation of an electronegative substituent at the anomeric position, and the axial lone pair of the ring oxygen is less susceptible to 1,3-diaxial repulsions than the axial hydrogen atom of cyclohexanes.[6] In this regard, we have demonstrated that hinge sugars, 1,3-disubstituted-2,4-diamino-2,4-dideoxy-β-D-xylopyranosides, which assume a $^4C_1$ conformation, undergo a ring flip between $^4C_1$ and $^1C_4$ structures by addition of a metal ion (Fig. 2A).[7] This ring flip is accompanied by a hinge-like motion with regard to the 1,3-substituents, which is applicable to molecular devices and tools, as imagined from their macro counterparts, such as pliers, tongs, and cams in a clock. In a preliminary communication,[8] we have demonstrated the potential of hinge sugars as movable components of molecular devices by applying it to a tong-like excimer fluorescence sensor (**1**), in which the pivot xylopyranoside assumes a $^1C_4$ conformation together with sterically demanding four axial substituents when a metal ion is bound (Fig. 2B). Although the report described the selectivity of the sensor for metal ions and evidence of the conformational change of the hinge sugar, the stacking effect of pyrene groups, attached at the 1- and 3-positions of the hinge sugar as an excimer fluorescence source,[9] was not fully discussed. The present paper describes full details of the preliminary report and additional studies regarding the effect of acids.

† Electronic supplementary information (ESI) available: general experimental procedures, fluorescence experiments and Figures S1–S32: ^{13}C and ^{1}H NMR, COSY, HMBC and HMQC spectra. See http://www.rsc.org/suppdata/ob/b4/b411344f/

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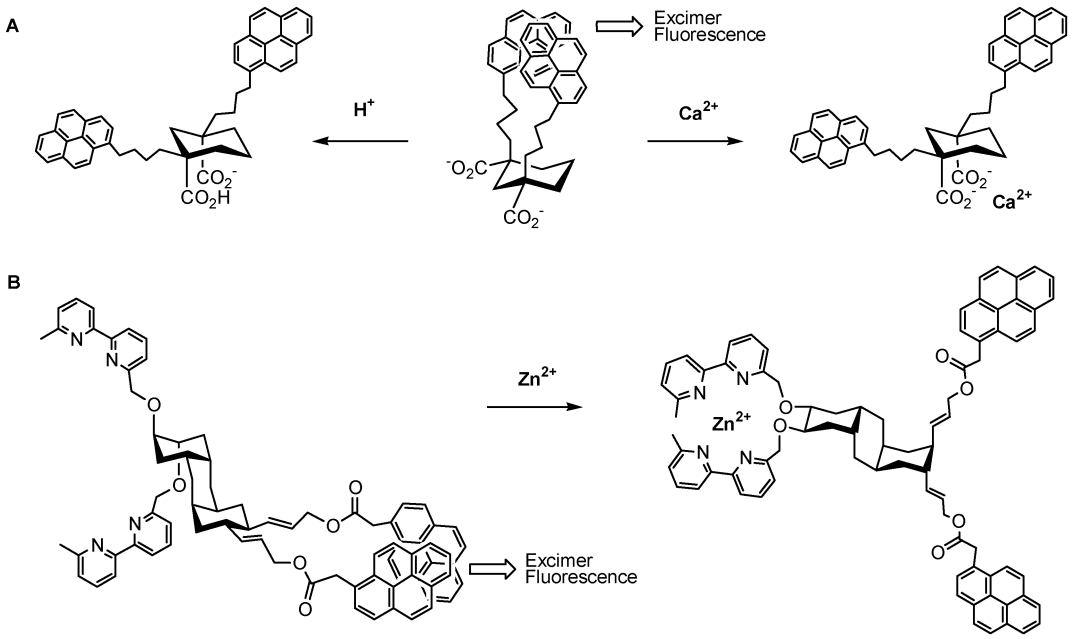


Fig. 1 The ring flip of cyclohexanes used for excimer fluorescence sensors of ions: (A) Smith's H^+ and Ca^{2+} sensor and (B) Koert's Zn^{2+} sensor.[4]

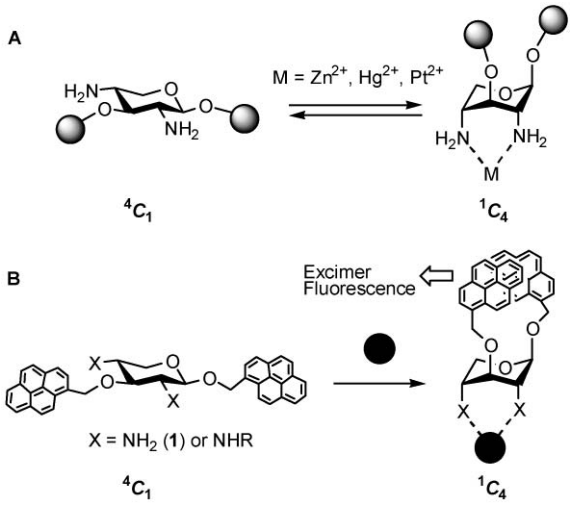


Fig. 2 2,4-Disubstituted-xylopyranosides as movable components of molecular devices: (A) chelation-driven hinge sugar and (B) a design of excimer fluorescence sensors based on a hinge sugar.

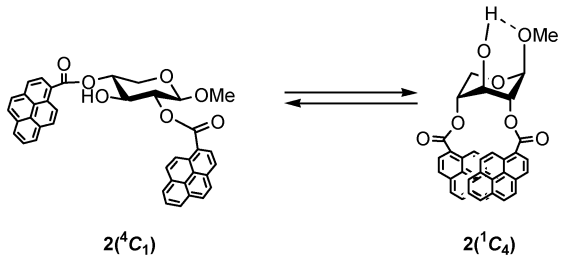


Fig. 3 Solvent-dependent conformational change of methyl 2,4-di-*O*-pyrenecarbonyl-β-D-xylopyranoside (**2**).

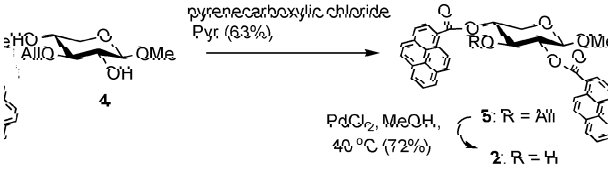
Results and discussion

Preliminary tests for the mobility of a xylopyranoside bearing pyrene groups

There was a potential problem with using hinge sugars as components of tong-like excimer fluorescence sensors: even an unsubstituted hinge sugar gives insufficient formation of the $^1C_4$ structure (at most 40% by chelation to Zn^{2+}).[7] This poor $^1C_4$ formation is fatal for the tong-like excimer fluorescence sensor, because sensitivity to an analyte is reduced by the poor excimer complex formation owing to the restriction of $^1C_4$ formation. We thus investigated at first whether the attachment of pyrene groups to a xylopyranoside is beneficial to its $^1C_4$ formation.

We selected an easy-to-synthesize model compound, methyl 2,4-di-*O*-pyrenecarbonyl-β-D-xylopyranoside (**2**), for the assessment of $^1C_4$ stability (Fig. 3). ^{1}H NMR measurement of an analogous derivative without a pyrene group, methyl 2,4-di-*O*-acetyl-β-D-xylopyranoside (**3**), have shown that the compound exists in equilibrium between $^1C_4$ (43%) and $^4C_1$ (57%) conformations in $CDCl_3$.[10] Thus, comparison of the populations of the $^1C_4$ structures of **2** and **3** would clarify the effect of pyrene groups on the stability of the $^1C_4$ structure.

Pyrenecarbonylation of methyl 3-*O*-allyl-β-D-xylopyranoside **4**[11] gave compound **5**, which was subsequently deallylated to give compound **2** (Scheme 1). Apparently from the ^{1}H NMR spectrum of **2** in $CDCl_3$ (Fig. 4A), the coupling patterns are totally distinctive from those expected for a $^4C_1$ conformation, indicating an equilibrium between $^4C_1$ and $^1C_4$ conformations. From the *J*-values (Table 1), $^1C_4$ population was calculated to be 93%. In the same way, the $^1C_4$ population for the 3-*O*-allylated compound **5** in $CDCl_3$ was found to be 81%. These $^1C_4$ populations are higher than that of **3** (43%), revealing that the 1,3-diaxial pyrene groups assist the formation of a $^1C_4$ structure, probably due to a stacking attractive force. The gained stability of the $^1C_4$ structure of the dipyrenecarboxylate **2** compared to the diacetate **3** is probably due to a stacking energy, which is calculated to be 1.7 kcal mol^{-1}.



Scheme 1

The IR spectrum of **2** in CCl_4 indicates an absorption band at 3530 cm^{-1} (Fig. 5), which is attributed to the OH stretching vibration with an intramolecular hydrogen bond creating a six-membered ring[13] as depicted in structure **2**($^1C_4$), suggesting OH3–O1 hydrogen bonding as a stabilizing factor of the $^1C_4$

Table 1 J-values (Hz) and calculated $^1C_4$ populations (%) of compounds **2** and **5** in various solvents

Compound	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$^1C_4$[a]
2	$CDCl_3$	2.1	4.0	4.0	2.6	2.3	93
2	CD_3OD	4.3	5.5	—[b]	—[b]	5.3	64
2	DMSO-d_6	6.7	8.2	8.2	4.7	9.0	22
5	$CDCl_3$	3.0	4.3	4.3	2.6	3.3	81

[a] Population (%) of $^1C_4$ conformation, calculated by a multiple regression analysis with a least squares fitting of the J-values calculated for model structures to the observed ones. The calculated J-values were derived by the generalized Karplus equation[12] from the dihedral angles of the computed $^4C_1$, $^1C_4$, $^2S_0$, $^3S_1$ and ^{03}B structures optimized by PC Spartan Plus software (Wavefunction Inc.) using SYBYL force field. The populations for the skew and boat conformations were negligible. [b] Not determined owing to multiplicity of the signals.

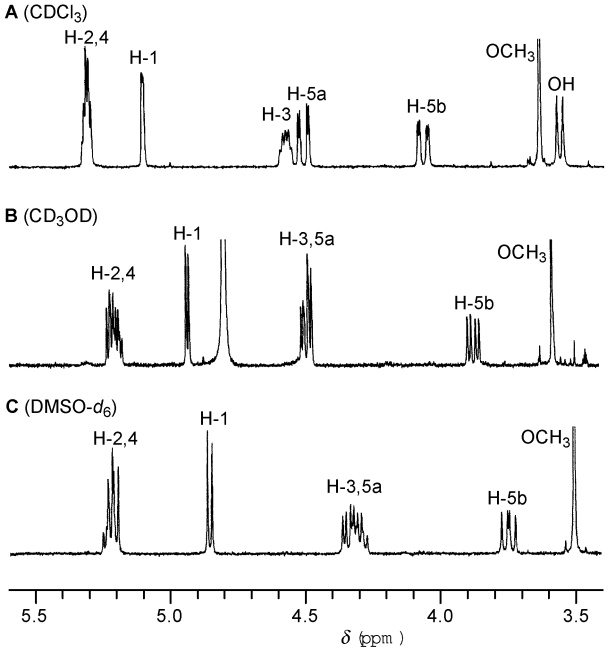


Fig. 4 400 MHz ^{1}H NMR spectra of compound **2** in various solvents (19.1 mM at 25 °C): (A) in $CDCl_3$, (B) in CD_3OD, and (C) in DMSO-d_6.

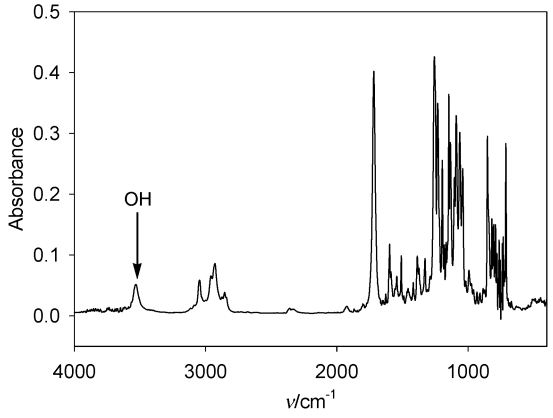


Fig. 5 IR spectrum of compound **2** (10 mM) in CCl_4.

structure. The same suggestion has been made with a $^1C_4$-stabilizing factor for compound **3**, based on its IR spectrum.[13] Compound **2** predominantly assumes a $^1C_4$ structure in CCl_4, since there were no detectable $^4C_1$-derived bands, such as *ca.* 3620 cm^{-1} for the hydrogen-bond-free OH3, *ca.* 3590 cm^{-1} for OH3–O2 or OH3–O4 creating a five-membered ring, and/or *ca.* 3490 cm^{-1} for OH3–O=C2 or OH3–O=C4. This result is consistent with that of ^{1}H NMR in $CDCl_3$, which reveals only 7% $^4C_1$ population. The OH3–O1 intramolecular hydrogen bond plays a role in stabilizing the $^1C_4$ structure of **2** to an extent that removal of the 3-*O*-allyl group of compound **5** increases $^1C_4$ population by 12%, which corresponds to a stabilization energy of 0.7 kcal mol^{-1}.

Given that hydrogen bonding is a stabilizing factor for the $^1C_4$ structure of **2**, a polar solvent such as DMSO or methanol would decrease the $^1C_4$ population to some extent by perturbing hydrogen bonds.[14] The ^{1}H NMR spectra of **2** in CD_3OD (Fig. 4B) and DMSO-d_6 (Fig. 4C) exhibited larger coupling constants compared with those of the $CDCl_3$ solution and $^1C_4$ populations of 64% in CD_3OD and 22% in DMSO-d_6 were computed from the J-values (Table 1). The gained stability of the $^1C_4$ structure in $CDCl_3$ compared with that in DMSO-d_6 is calculated to be 2.3 kcal mol^{-1}, much larger than expected from the hydrogen bond alone. Interestingly, this value is approximately the sum of the hydrogen bond energy (0.7 kcal mol^{-1}) and the pyrene stacking energy (1.7 kcal mol^{-1}) estimated above. This result suggests that not only hydrogen bonding but also stacking of pyrene groups was cancelled out by the polar solvent. Since the π-stacking is an electrostatic interaction,[15] it is rational to suppose that the polar solvent neutralized the charges that would produce the attractive force. As a consequence, the $^1C_4$ structure of compound **2** is unexpectedly stable owing to pyrene stacking, which in turn resolves the potential awkwardness of hinge sugars as movable components of tong-like sensors.

As a second step in the preliminary tests, we measured fluorescence spectra of compound **2** in various solvents to confirm that excimer fluorescence appears only in the $^1C_4$ structure due to an intramolecular stacking of pyrene groups and not due to intermolecular interactions. Fig. 6 shows the fluorescence spectra with excitation at 355 nm for 1 μM solutions of **2** in DMSO, methanol, and $CHCl_3$. The lower limit of the concentration of **2** to observe excimer fluorescence was 10 nM in $CHCl_3$. Fluorescence peaks due to the pyrene monomer were observed at *ca.* 400 nm. Excimer fluorescence at *ca.* 500 nm was significant in $CHCl_3$, barely seen in methanol, and null in DMSO. These results were in good accordance with the ^{1}H NMR measurements: nonpolar solvents tend to afford the $^1C_4$ structure to a greater extent, which allocates the two pyrene groups in a diaxial and parallel orientation to afford excimer fluorescence. Polar solvents such as MeOH and DMSO decrease excimer fluorescence, because the stacking of pyrene groups and the hydrogen-bonding are cancelled out in these solvents.

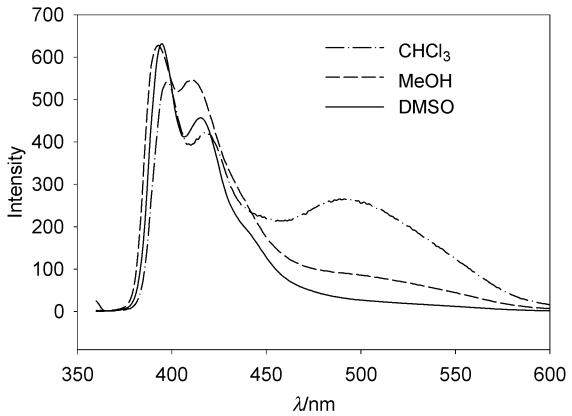
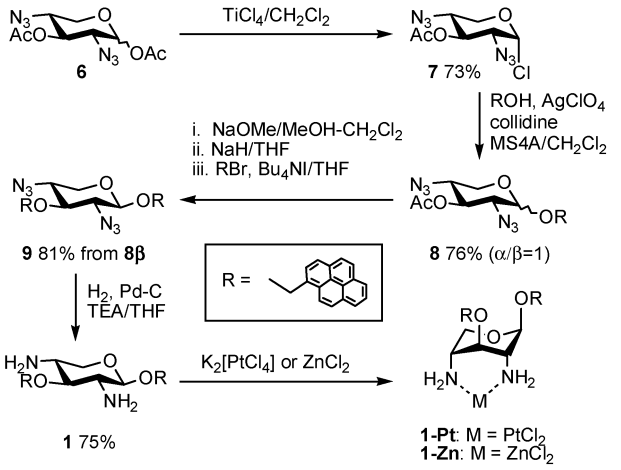


Fig. 6 Solvent-dependent excimer fluorescence of compound **2** (1 μM) with excitation at 355 nm. Intensity scales are five-fold for $CHCl_3$ solution and two-fold for CH_3OH solution.

Metal-ion-induced excimer fluorescence of a hinge sugar bearing pyrene groups

Since the pyrene groups attached to a xylopyranose are beneficial to its $^1C_4$ formation as demonstrated in the previous section,

xylopyranose–pyrene conjugates would find a number of applications as excimer fluorosensors. In this context, we designed 2,4-diamino-xylopyranoside **1** as a common component for various molecular sensors. The amino group of **1** can be a universal connector for various recognition components, while the diamino group can be also a metal chelator. Compound **1** was synthesized from 2,4-diazido-xylopyranose **6** (Scheme 2). Compound **6**[7] was converted to glycosyl chloride **7** with $TiCl_4$, which was then subjected to typical glycosidation conditions to give pyrenylmethyl xyloside **8**. Deacetylation and alkylation at O3 of compound **8** gave compound **9**, which was subjected to a reduction of the azido groups to give the desired compound **1**.



Scheme 2

NMR measurements revealed that compound **1** assumed a $^4C_1$ conformation in all solvents tested, *i.e.*, $CDCl_3$, acetone-d_6, DMF-d_7 and DMSO-d_6. With fluorescence spectroscopy, however, $CHCl_3$ and DMF solutions of **1** (1 μM) afforded a gradual evolution of excimer fluorescence over 12 h as shown in Fig. 7. We found that the excimer fluorescence development was owing to exposure to the light, and storage of $CHCl_3$ solution of **1** in the dark caused hardly any excimer fluorescence after 12 h. This fluorescence development was concentration-dependent and did not occur with the higher concentrations required for ^{1}H NMR measurements (>0.5 mM). The excimer fluorescence, once developed, did not disappear even after 24 h storage in the dark. The fluorescence spectra for the acetone and DMSO solutions did not exhibit excimer fluorescence even after a long exposure to the light, and thus these solvents were used for metal addition experiments.

First of all, Pt^{2+}, Mn^{2+} and Zn^{2+} were added to the solution of **1** in DMSO. While addition of two equivalents of either $Zn(OAc)_2$ nor $Mn(OAc)_2$ did not give any significant spectral changes, an equivalent of $K_2[PtCl_4]$ induced an increase of excimer fluorescence over 24 h as shown in Fig. 8. The slow spectral change is consistent with a slow formation of a Pt^{2+} complex with the hinge sugar as previously studied.[7] In practice, a ^{1}H NMR study revealed that the ring conformation of **1** in DMF-d_7 changed from $^4C_1$ to $^1C_4$ 15 h after addition of Pt^{2+}. Complex **1–Pt** was isolable and a complete assignment of ^{1}H NMR for the complex was possible by COSY, HMQC and HMBC measurements.

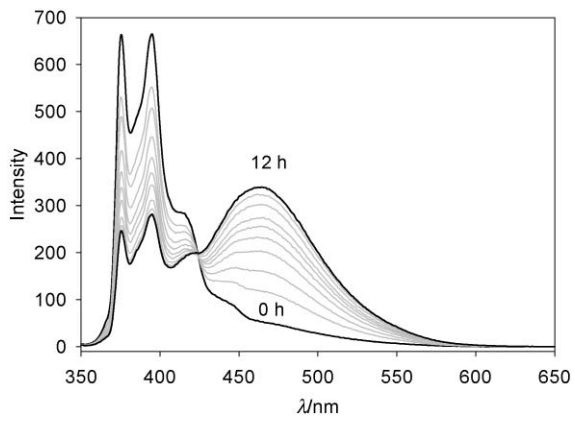


Fig. 7 Time evolution of excimer fluorescence for the 1 μM solution of compound **1** in DMF at 35 °C (excitation at 347 nm), monitored at 0, 1, 2, 3, 4, 5, 6, 8, 10, and 12 h.

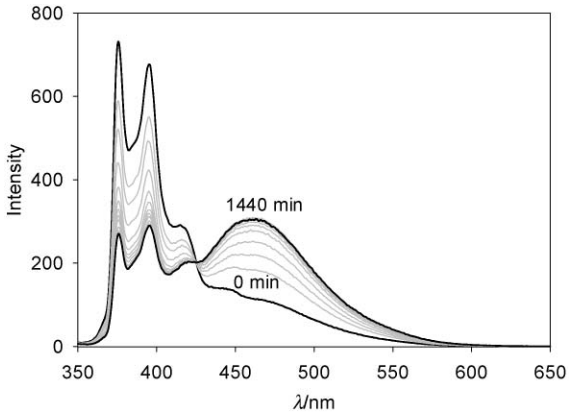


Fig. 8 Fluorescence spectral change of compound **1** (1 μM in DMSO; excitation at 347 nm) after addition of 1 equiv. of $K_2[PtCl_4]$. The reaction was monitored at 0, 30, 60, 120, 240, 360, 480, 600, 720, 960, 1200, and 1440 min.

The observation that Mn^{2+} and Zn^{2+} did not cause excimer complex formation in DMSO might be due to the masking of these metal ions by a sulfoxide coordination.[16] Thus, we next tested acetone as a less nucleophilic solvent for metal ions. The test was carried out with acetone solutions of 10 equivalents metal ions ($LiClO_4$, CF_3COONa, $Mg(ClO_4)_2$, $MnCl_2$, $FeCl_2{\cdot}4H_2O$, $FeCl_3$, $CoCl_2{\cdot}6H_2O$, $CuCl_2$, $ZnCl_2$, $AgClO_4$) or saturated acetone solutions of barely soluble metal ions ($CaCl_2$, $Cr(OAc)_3$, $NiCl_2$, $ZrCl_2$, $CdCl_2{\cdot}4H_2O$, $BaCl_2$, $La(OAc)_3$, $Pb(NO_3)_2$). Of these metal ions, Mg^{2+}, Mn^{2+}, Zn^{2+}, and Cd^{2+} induced excimer fluorescence, and Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zr^{2+} and Ag^+ merely quenched the fluorescence of a pyrene monomer at *ca.* 390 nm. Thus detailed titration experiments were performed for Mg^{2+}, Mn^{2+}, Zn^{2+} and Cd^{2+} ions (Fig. 9). It appears that induction of excimer fluorescence is much more effective with Cd^{2+} and Zn^{2+} compared to the other two ions. For small amounts of metal ions, however, only Zn^{2+} is superior to other ions as obviously demonstrated by the graph in Fig. 10, which shows the strength of excimer fluorescence at 458 nm relative to pyrene monomer fluorescence at 393 nm plotted against the amount of added metal ions. The minimum concentration of Zn^{2+} required to observe excimer fluorescence was 50 nM with 100 nM of **1**, comparable to most metal ion sensors of small molecules.[17] In the case of Mg^{2+}, Cd^{2+} and Mn^{2+}, there were slight drifts from isosbetic points as the concentrations of the metal ions increased. The decrease of total fluorescence for Cd^{2+} and Mn^{2+} is ascribed to quenching by high concentrations of transition metal ions.

^{1}H NMR showed that the addition of $ZnCl_2$ (5 equiv.) to the acetone-d_6 solution of **1** immediately and completely changed the conformation from $^4C_1$ into $^1C_4$ as indicated by their small ^3J-values (Fig. 11). The predominant $^1C_4$ formation was unexpected, because our previous studies demonstrated that the addition of Zn^{2+} to the aqueous solution of a simple hinge sugar derivative resulted in a $^4C_1$–$^1C_4$ equilibrium with a $^1C_4$ proportion of 40% at most.[7] As demonstrated with compound **2**, the stabilizing energy of the $^1C_4$ conformer by the stacking of two pyrene groups is about 1.7 kcal mol^{-1}, large enough to explain the predominant $^1C_4$ formation. On the other hand, compound **1** assumes a mostly $^4C_1$ conformation even in the

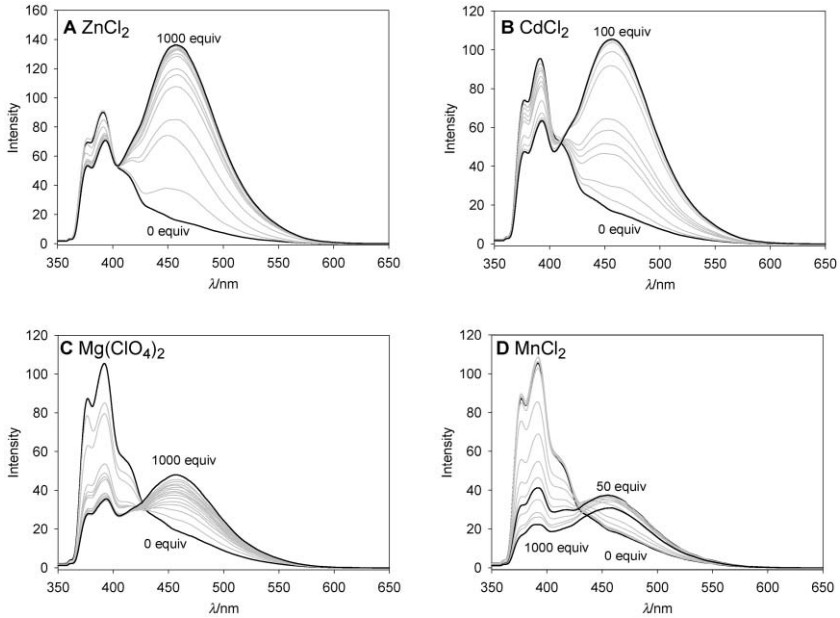


Fig. 9 Fluorescence spectral change of compound **1** (1 μM in acetone; excitation at 347 nm) with the addition of various metal ions (0, 0.5, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 100, 300, 500, and 1000 equiv.): (A) $ZnCl_2$, (B) $CdCl_2{\cdot}4H_2O$ (up to 100 equiv.), (C) $Mg(ClO_4)_2$, and (D) $MnCl_2$.

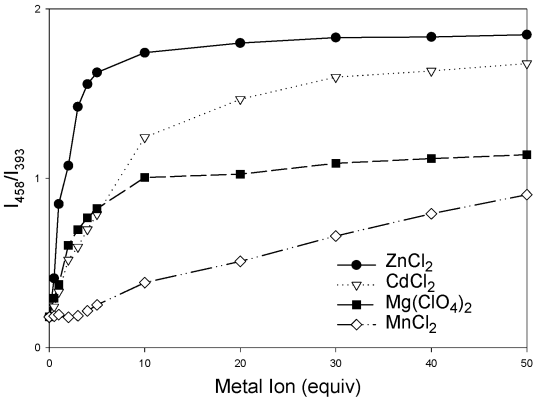


Fig. 10 Difference in the sensitivity of metal ion sensor **1** as shown by the change of relative intensities of excimer fluorescence (I_{458}/I_{393}) with the addition of metal ions (equiv.).

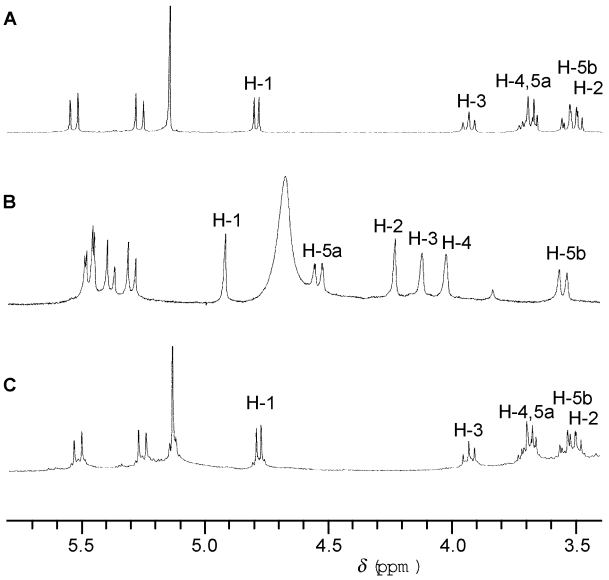


Fig. 11 400 MHz ^{1}H NMR spectra of compound **1** in acetone-d_6: (A) without additives ([**1**] = 16.3 mM at 18.8 °C), (B) with 5.0 equiv. $ZnCl_2$ ([**1**] = 16.3 mM at 18.8 °C), and (C) with 5.3 equiv. $ZnCl_2$ and then 5.3 equiv. of triethylenetetraamine ([**1**] = 18.0 mM at 18.1 °C).

presence of 9.8 equiv. of $Mg(ClO_4)_2$, while a dilute solution of the 1 : 10 mixture of **1** and Mg^{2+} caused a significant excimer fluorescence as shown in Fig. 9C. Probably, the concentrated solution for ^{1}H NMR makes the intramolecular stacking of pyrene groups more difficult than the dilute solution for the fluorescence measurement, and the weak chelation to Mg^{2+} is not enough for the $^1C_4$ conformation to persist.

The complex of **1** with Zn^{2+} observed in acetone-d_6 could not be isolated in contrast to the complex **1–Pt**: the acetone-d_6 solution was concentrated and partitioned between $CHCl_3$ and H_2O, and the $CHCl_3$ layer was concentrated and remeasured by ^{1}H NMR in acetone-d_6 to indicate a perfect recovery of the $^4C_1$ conformation. Recovery of the $^4C_1$ conformation was also possible by *in situ* addition of triethylenetetraamine (Fig. 11C). In accordance with ^{1}H NMR, the excimer fluorescence of **1** induced by 5 equiv. of Zn^{2+} is totally cancelled out by 5 equiv. of triethylenetetraamine.

Although compound **1** was designed as a metal ion sensor, we found that the addition of an adequate amount of acids to the $CHCl_3$ solution of **1** caused an excimer fluorescence formation as shown in Fig. 12. The maximum excimer fluorescence was obtained when 1 equiv. of trifluoromethanesulfonic acid (TfOH), 40 equiv. of trifluoroacetic acid (TFA), or 1000 equiv. of acetic acid (AcOH) was added. On the other hand, a large excess of acid extinguished excimer fluorescence. Conformational changes in the presence of acids could be followed by ^{1}H NMR as shown in Fig. 13. Addition of 1 equiv. trifluoroacetic acid-d caused stabilization of the $^1C_4$ conformation (63% in population), whereas the $^4C_1$ conformation was recovered by the addition of 10 equiv. of the acid. These phenomena are explained as follows. At a low [D^+], the amino group at the 2 position was preferentially deuterated as indicated by the larger downfield shift of H2 than H4 in ^{1}H NMR. The resultant ammonium ion is a strong hydrogen-bond donor to the amino group at the 4 position, constructing a bridged $^1C_4$ structure as shown in Fig. 14. An excess amount of the acid caused a further deuteration at N4 and the downfield shift of H4 in ^{1}H NMR. With this second deuteration, the bridged hydrogen bond was broken and the ammonium ions repelled each other to end in the recovery of the $^4C_1$ structure.

In conclusion, we created a hinge sugar-based sensor **1**, which produces excimer fluorescence by chelation to ions like Zn^{2+},

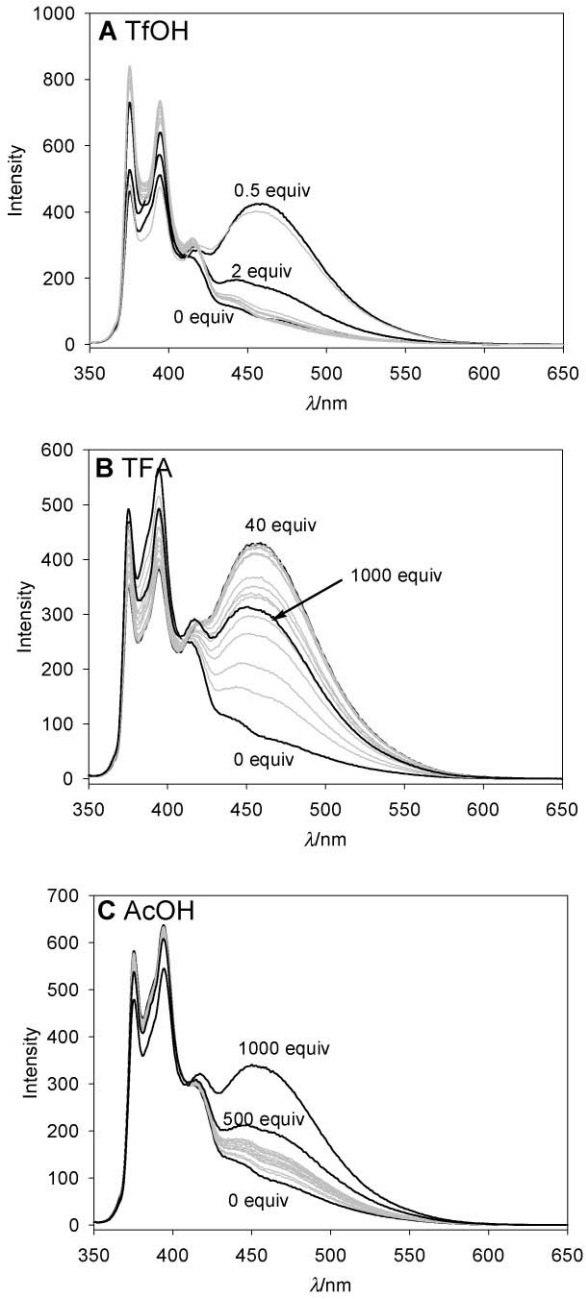


Fig. 12 Fluorescence spectral change of compound **1** (1 μM in $CHCl_3$; excitation at 347 nm) with the addition of various acids (0, 0.5, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 100, 300, 500, and 1000 equiv.): (A) trifluoromethanesulfonic acid (TfOH), (B) trifluoroacetic acid (TFA), and (C) acetic acid (AcOH).

Cd^{2+}, Mg^{2+}, Mn^{2+} and H^+. We also demonstrated that the stacking of pyrene groups assists the $^1C_4$ conformation of **1**, as well as that of 2,4-dipyrenyl-xylopyranoside **2**. This finding extends the scope of hinge sugars as movable components. Since the amino group of **1** can be a connector for a variety of analyte binding groups, such as boronic acids for sugars,[18] polyamides for DNA minor grooves,[19] and sugar ligands for sugar-receptors,[20] **1** is a versatile component for molecular devices and sensors. The sensor also provides a facile system to evaluate the conformational change of hinge sugars, with which the conformational changes can be studied quickly and sensitively.

Experimental

General

All solvents and reagents used were reagent grade and, in cases where further purification was required, standard procedures

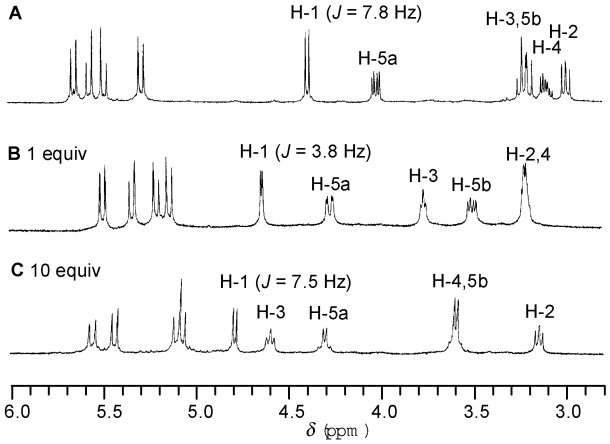


Fig. 13 400 MHz ^{1}H NMR spectra of compound **1** in $CDCl_3$ (11.1 mM at 18.5 °C): (A) without additives, (B) with 1.0 equiv. trifluoroacetic acid-*d* (TFA-*d*), and (C) with 10 equiv. TFA-*d*.

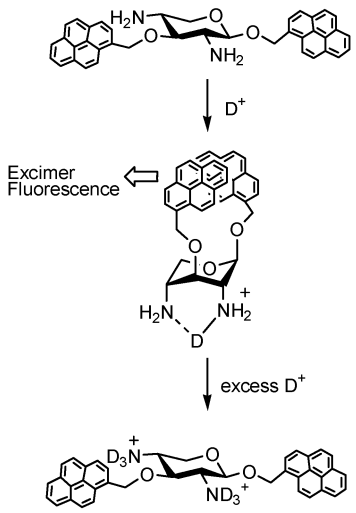


Fig. 14 Conformational changes of compound **1** by addition of proton. All the hydrogen atoms depicted are replaced with deuterium atoms in ^{1}H NMR experiments.

were followed.[21] Solution transfers where anhydrous conditions were required were done under dry argon using syringes. Thin-layer chromatograms (TLC) were performed on precoated silica gel Merck 60-F254 plates (Art 5715) and visualized by quenching of fluorescence and/or by charring after spraying with 1% $CeSO_4$–1.5% $(NH_4)6Mo_7O_{24}{\cdot}4H_2O$–10% H_2SO_4. Column chromatography was performed on Merck Kieselgel 60 (Art 7734), Wako gel C-300, or Kanto Silica gel 60N (spherical, neutral) with the solvent systems specified.

Optical rotations were determined with a Horiba SEPA-200 or JASCO DIP-4 polarimeter using a 1 dm or 0.1 dm length cell. ^{1}H NMR (1D, COSY, HMQC, and HMBC) spectra were recorded at 400 MHz (Varian Unity-400) or 270 MHz (JEOL EX-270). Internal tetramethylsilane (δ 0 ppm) was used as a standard in $CDCl_3$ or solvents peaks were used as standards (δ 2.05 ppm in acetone-d_6, δ 2.50 ppm in DMSO-d_6 or δ 2.75 in DMF-d_7). Chemical shifts are expressed in ppm referenced to the solvent, as an internal standard. The multiplicity of signals is abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, ddd = doublet of doublets of doublets, br = broad signal, m = multiplet. ^{13}C NMR spectra were recorded at 67.8 MHz (JEOL JNM-EX-270) or 100.6 MHz (Varian Unity-400) and solvents peaks were used as standards (δ 77.0 ppm in $CDCl_3$, δ 29.8 ppm in acetone-d_6 or δ 29.76 in DMF-d_7). High resolution mass spectra (HRMS) were recorded on a Mariner Biospectrometry Workstation ESI-TOF MS. Fourier transform infrared spectra were obtained with a

Shimadzu FTIR-8400S, in which a 10 mM solution in CCl_4 was measured in a cell with 0.5 mm length.

General fluorescence experiments

Fluorescence spectra were recorded at 35 °C on a Shimadzu RF-5300PC fluorophotometer with excitation at 355 nm for **2** (1 μM) and 347 nm for **1** (1 μM), sampling intervals of 2 nm for **2** and 1 nm for **1**, excitation band widths of 3 nm for **2** and 1.5 nm for **1**, and an emission band width of 5.0 nm for both compounds. A cell with 10 mm width and 3 mm depth was used.

1) Titration: to a thermostated (35 °C) solution of **1** (1 μM, 1 mL) were dropped appropriate amounts of the solution of a metal ion and **1** (1 μM), and the fluorescence spectrum was recorded at specified amounts of the metal ion.

2) Time course: to a thermostated (35 °C) solution of **1** (2 μM) in DMSO (500 μL) was added a solution of $K_2[PtCl_4]$ (2 μM) in DMSO (500 μL), and the fluorescence spectrum was recorded at appropriate time intervals.

Synthesis of 1, 2 and 7–9

Methyl 3-*O*-allyl-2,4-di-*O*-(1-pyrenecarbonyl)-β-D-xylopyranoside, 5. A solution of 1-pyrenecarboxylic acid (549.0 mg, 2.23 mmol) in $SOCl_2$ (20 mL) was refluxed for 3 h and then concentrated under reduced pressure. The residue was dissolved in pyridine (6 mL) at 0 °C and a solution of methyl 3-*O*-allyl-β-D-xylopyranoside (**4**) (85.7 mg, 0.422 mmol) in pyridine (2 mL) was added. After stirring for 8 h, water and $CHCl_3$ were added to the reaction mixture. The organic layer was washed with 0.5 M HCl and 1 M NaOH, dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (hexane–ethyl acetate, 10 : 1 to 6 : 1) to give **5** (175.0 mg, 63%) as crystals. R_f 0.16 (hexane–ethyl acetate, 6 : 1); mp 214–216 °C (from EtOH); $[\alpha]_D^{23}$ −43.6 (*c* 1.0 in $CHCl_3$); δ_H (270 MHz; $CDCl_3$; Me_4Si) 3.60 (3H, s, OMe), 3.95 (1H, dd, *J* 3.3, *J* 12.5, 5-Ha), 4.28 (1H, t, *J* 4.3, 3-H), 4.42–4.45 (2H, m, C*H*$_2$–CH=CH$_2$), 4.55 (1H, dd, *J* 2.6, *J* 12.5, 5-Hb), 4.98 (1H, d, *J* 3.0, 1-H), 5.22–5.46 (4H, m, CH$_2$–CH=C*H*$_2$, 2-H, 4-H), 5.95–6.10 (1H, m, CH$_2$–C*H*=CH$_2$), 7.41–9.07 (18H, m, Ar); δ_C (67.8 MHz; $CDCl_3$) 56.2, 59.1, 69.1, 69.6, 72.1, 73.4, 77.2, 99.9, 118.0, 122.5, 122.6, 123.5, 123.6, 124.2, 124.3, 124.4, 125.9, 126.0, 126.1, 126.6, 126.7, 128.1, 128.3, 129.3, 129.4, 129.5, 129.9, 130.6, 130.6, 130.9, 134.0, 134.1, 134.2, 166.6, 167.1; HRMS (ESI) Found: 683.2067 [M + Na]$^+$. Calc. for $C_{43}H_{32}O_7Na$: 683.2046.

Methyl 2,4-di-*O*-(1-pyrenecarbonyl)-β-D-xylopyranoside, 2. The solution of **5** (35.1 mg, 0.053 mmol) and $PdCl_2$ (2.0 mg, 0.01 mmol) in methanol (1 mL) was stirred for 3 h at 40 °C. The insoluble material was filtered off with Celite and the filtrate was concentrated. The residue was purified by silica gel chromatography (hexane–ethyl acetate, 3.5 : 1 to 3 : 1) to give **2** (23.7 mg, 72%) as yellow crystals: R_f 0.17 (hexane–ethyl acetate, 3 : 1); mp 82–86 °C (from EtOH), $[\alpha]_D^{23}$ –25.0 (*c* 1.0 in $CHCl_3$); δ_H (400 MHz; $CDCl_3$; Me_4Si; 298 K) 3.57 (1H, d, OH), 3.63 (3H, s, OMe), 4.07 (1H, dd, $J_{4,5a}$ 2.3 Hz, 5-Ha), 4.52 (1H, dd, $J_{4,5b}$ 2.6, $J_{5a,5b}$ 13.3, 5-Hb), 4.58 (1H, dt, $J_{2,3} = J_{3,4}$ 4.0, $J_{3,OH}$ 8.9, 3-H), 5.11 (1H, d, $J_{1,2}$ 2.1, 1-H), 5.30–5.33 (2H, m, 2-H, 4-H), 7.34–9.02 (18H, m, Ar); δ_H (400 MHz; CD_3OD; 298 K) 3.57 (3H, s, OMe), 3.87 (1H, dd, $J_{4,5a}$ 5.3, $J_{5a,5b}$ 12.4, H-5a), 4.55–4.47 (2H, m, 3-H, 5-Hb), 4.94 (1H, d, 1-H), 5.20 (1H, dt, 4-H), 5.23 (1H, dd, $J_{1,2}$ 4.3, $J_{2,3}$ 5.5, 2-H), 7.63–8.93 (18H, m, Ar); δ_H (400 MHz; DMSO-d_6; 298 K) 3.50 (3H, s, OMe), 3.75 (1H, dd, $J_{4,5a}$ 9.0, 5-Ha), 4.31 (1H, dt, $J_{2,3}$ 8.2, $J_{3,4}$ 8.2, 3-H), 4.35 (1H, dd, $J_{4,5b}$ 4.7, $J_{5a,5b}$ 11.6, H-5b), 4.86 (1H, d, $J_{1,2}$ 6.7, 1-H), 5.20–5.24 (2H, m, 2-H, 4-H), 6.09 (1H, d, $J_{3,OH}$ 5.8, OH), 8.13–9.13 (18H, m, Ar); δ_C (67.8 MHz; $CDCl_3$) 56.2, 58.5, 66.8, 69.7, 70.6, 77.2, 99.5, 122.2, 122.7, 123.4, 123.5, 123.5, 124.1, 124.1, 124.3, 125.8, 126.0, 126.0, 126.1, 126.5, 126.5, 128.2, 128.3, 129.1, 129.2, 129.4, 129.4, 129.9, 130.5, 130.7, 130.8, 133.9, 134.0, 166.9, 167.3; HRMS (ESI) Found: 643.1784 [M + Na]$^+$. Calc. for $C_{40}H_{28}O_7Na$ 643.1733.

3-*O*-Acetyl-2,4-diazido-2,4-dideoxy-α-D-xylopyranosyl chloride, 7. To a stirred solution of compound **6** (871 mg, 3.06 mmol) in dichloromethane (18 mL) was slowly added titanium tetrachloride (670 μL, 6.13 mmol) under argon and the solution was stirred for 3 h at room temperature. The solution was diluted with chloroform and washed with water and aqueous sodium bicarbonate. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (hexane–ethyl acetate, 4 : 1) to give **7** (619 mg, 73%) as a syrup. R_f 0.23 (hexane–ethyl acetate, 4 : 1); $[\alpha]_D^{23}$ +210.2 (*c* 1.0 in $CHCl_3$); Found: C, 32.5; H, 3.5; N, 32.45; Cl, 13.4. Calc. for $C_7H_9ClN_6O_3$: C, 32.3; H, 3.5; N, 32.2; Cl, 13.6%; δ_H (270 MHz; $CDCl_3$; Me_4Si; 298 K) 2.20 (3H, s, COMe), 3.63–3.73 (2H, m, 2-H, 4-H), 3.89 (1H, t, $J_{4,5a}$ 11.2, 5-Ha), 3.97 (1H, dd, $J_{4,5b}$ 6.3, $J_{5a,5b}$ 11.9, 5-Hb), 5.46 (1H, t, $J_{2,3} = J_{3,4}$ 9.9, 3-H), 6.08 (1H, d, $J_{1,2}$ 3.6, 1-H); δ_C (67.8 MHz; $CDCl_3$; Me_4Si) 20.6 (OMe), 58.9 (C-2), 62.1 (C-5), 62.5 (C-4), 70.6 (C-3), 92.4 (C-1), 169.4 (C=O).

1-Pyrenylmethyl 3-*O*-acetyl-2,4-diazido-2,4-dideoxy-α,β-D-xylopyranoside, 8α and 8β. The mixture of 1-pyrenemethanol (361 mg, 1.55 mmol), $AgClO_4$ (193 mg, 0.93 mmol), 2,4,6-collidine (120 μL, 0.93 mmol) and molecular sieves 4 Å (200 mg) in dichloromethane (6 mL) was stirred for 1 h under argon at room temperature in a light-shielded flask. To the mixture was added compound **7** (203 mg, 0.78 mmol) in dichloromethane (4 mL) and the mixture was stirred for a further 16 h at room temperature. The mixture was filtered through Celite, and the filtrate was diluted with chloroform and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (hexane–chloroform, 1 : 3) and by recrystallization from hexane–ethyl acetate (2 : 1) to give **5**β (115 mg, 33%) as crystals. The mother liquor was further chromatographed on a column of silica gel (C300, hexane–ethyl acetate, 3 : 1) to give **8**β (16 mg, 5%) and **8**α (132 mg, 38%) as solids.

8α: R_f 0.34 (hexane-ethyl acetate = 3:1); mp 125–126 °C (from EtOH); $[\alpha]_D^{26}$ +194.5 (*c* 0.8 in $CHCl_3$); Found: C, 62.3; H, 4.5; N, 17.9. Calc. for $C_{24}H_{20}N_6O_4$ 1/3H_2O: C, 62.3; H, 4.5; N, 18.2%.; δ_H (270 MHz, $CDCl_3$; Me_4Si) 2.15 (3H, s, COMe), 3.08 (1H, dd, 2-H), 3.58–3.80 (3H, m, 4-H, 5-Ha, 5-Hb), 5.02 (1H, d, $J_{1,2}$ 3.3, 1-H), 5.02, 5.29 (1H × 2, d × 2, *J* 12.5, CH_2Ar), 5.49 (1H, t, $J_{2,3} = J_{3,4}$ 9.23, 3-H), 7.98–8.38 (9H, m, Ar); δ_C (67.8 MHz; $CDCl_3$; Me_4Si) 20.7, 59.8, 59.9, 61.0, 67.7, 70.7, 96.5, 123.0, 124.5, 124.6, 124.8, 125.5, 126.0, 127.3, 127.6, 127.8, 128.2, 128.8, 129.5, 130.7, 131.9, 131.7, 169.7.

8β: R_f 0.35 (hexane–ethyl acetate = 3 : 1); mp 176–177 °C (from EtOH); $[\alpha]_D^{25}$ +14.6 ° (*c* 0.8 in $CHCl_3$); Found: C, 62.6; H, 4.5; N, 18.0. Calc. for $C_{24}H_{20}N_6O_4$ 1/3H_2O: C, 62.3; H, 4.5; N, 18.2%; δ_H (270 MHz, $CDCl_3$; Me_4Si) 2.17 (3H, s, COMe), 3.22 (1H, t, 5-Ha), 3.46 (1H, dd, 2-H), 3.63 (1H, ddd, $J_{4,5a}$ 10.9, 4-H), 4.13 (1H, dd, $J_{4,5b}$ 5.6, $J_{5a,5b}$ 12.2, 5-Hb), 4.41 (1H, d, $J_{1,2}$ 7.9, 1-H), 4.82 (1H, t, $J_{2,3} = J_{3,4}$ 9.9, 3-H), 5.37, 5.65 (1H × 2, d × 2, *J* 11.5, CH_2Ar), 8.00–8.40 (9H, m, Ar); δ_C (67.8 MHz; $CDCl_3$; Me_4Si) 20.8, 59.3, 63.9, 64.0, 69.5, 72.8, 100.7, 122.9, 124.5, 124.5, 124.8, 125.4, 126.0, 127.2, 127.6, 127.7, 128.0, 128.7, 129.6, 130.6, 131.1, 131.7, 169.5.

1-Pyrenylmethyl 3-*O*-(1-pyrenylmethyl)-2,4-diazido-2,4-dideoxy-β-D-xylopyranoside, 9. To a stirred solution of compound **8**β (165 mg, 0.36 mmol) in dichloromethane–methanol (7 : 2 v/v, 9 mL) was dropped 100 mM sodium methoxide (0.7 mL, 0.07 mmol) at room temperature. After 12 h, the solution was neutralized by Dowex50WX-8(H^+) and concentrated. The residue was dissolved in a solution of Bu_4NI (15 mg, 0.04 mmol) in THF (4.5 mL) and the resultant solution was dropped into a stirred suspension of NaH (26 mg, 1.08 mmol) in THF (4 mL) at 0 °C. After stirring for 40 min at room temperature, a solution

of 1-pyrenemethyl bromide (160 mg, 0.54 mmol) in THF (4 mL) was added and stirred for a further 2 h at room temperature. Ice-cold water was added and the mixture was extracted with $CHCl_3$. The organic layer was washed with saturated ammonium chloride and brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane–chloroform, 1 : 2) to give **9** (184 mg, 81%) as a yellow solid. R_f 0.35 (hexane–ethyl acetate, 4 : 1); mp 220–220.5 °C (from EtOH); $[\alpha]_D^{26}$ +100.0 (*c* 0.4 in THF); Found: C, 74.4; H, 4.7; N, 12.7. Calc. for $C_{39}H_{28}N_6O_3$: C, 74.5; H, 4.5; N, 13.4%; δ_H (270 MHz, $CDCl_3$; Me_4Si) 3.14 (1H, t, 5-Ha), 3.28 (1H, t, 3-H), 3.52 (1H, dd, $J_{2,3}$ 9.6, 2-H), 3.63 (1H, ddd, $J_{3,4}$ 9.6, $J_{4,5a}$ 10.9, 4-H), 4.09 (1H, dd, $J_{4,5b}$ 5.6, $J_{5a,5b}$ 11.9, 5-Hb), 4.34 (1H, d, $J_{1,2}$ 7.9, 1-H), 5.38, 5.38, 5.55, 5.66 (1H×4, d×4, *J* 10.5, CH_2Ar), 7.96–8.45 (18H, m, Ar); δ_C (67.8 MHz; $CDCl_3$; Me_4Si) 61.2, 64.1, 66.3, 69.1, 73.5, 81.1, 100.7, 123.2, 124.5, 124.6, 124.7, 124.9, 125.3, 125.4, 125.5, 125.9, 126.1, 127.4, 127.6, 127.8, 127.8, 128.1, 129.1, 129.6, 129.8, 130.3, 130.8, 130.8, 131.2, 131.2, 131.6, 131.8.

1-Pyrenylmethyl 3-*O*-(1-pyrenylmethyl)-2,4-diamino-2,4-dideoxy-β-D-xylopyranoside, 1. The solution of compound **9** (20 mg, 0.03 mmol), triethylamine (3 μL, 0.016 mmol) and 10% Pd/C (3 mg) in THF (1.6 mL) was stirred for 10 h under H_2 gas at room temperature. After the insoluble materials were removed by Celite filtration, the filtrate was concentrated. The residue was purified by silica gel chromatography (C300, chloroform–methanol–aqueous NH_3, 1 : 0 : 0 to 30 : 1 : 0.15) to give **1** (14 mg, 75%) as a yellow solid. R_f 0.23 (chloroform–methanol, 20 : 1); mp 118.5–120 °C (from EtOH); $[\alpha]_D^{28}$ −59.7 (*c* 0.7 in $CHCl_3$); δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.0 (1H, dd, 2-H), 3.10 (1H, ddd, 4-H), 3.20 (1H, t, $J_{4,5a}$ 10.8, 5-Ha), 3.23 (1H, t, $J_{2,3} = J_{3,4}$ 9.3, 3-H), 4.02 (1H, dd, $J_{4,5b} = 4.9$, $J_{5a,5b} = 11.4$, 5-Hb), 4.39 (1H, d, $J_{1,2}$ 7.8, 1-H), 5.29, 5.47, 5.55, 5.65 (1H × 4, d × 4, *J* 11.4, 11.6, CH_2Ar), 7.99–8.43 (18H, m, Ar); δ_H (400 MHz; acetone-d_6) 3.49 (1H, t, 2-H), 3.52 (1H, dd, $J_{4,5a}$ 9.5, $J_{5a,5b}$ 11.6, 5-Ha), 3.64–3.71 (2H, m, 4-H, 5-Hb), 3.91 (1H, t, $J_{2,3}$ 9.5, $J_{3,4}$ 8.2, 3-H), 4.73 (1H, d, $J_{1,2}$ 7.6, 1-H), 5.06 (2H, 2s, CH_2Ar), 5.17 (1H, d, *J* 11.7, CH_2Ar), 5.42 (1H, d, *J* 11.7, CH_2Ar), 7.79–8.28 (m, 18H, Ar); δ_H (400 MHz; DMSO-d_6) 2.70 (1H, t, H-2), 2.86 (1H, ddd, 4-H), 3.16 (1H, t, $J_{4,5a}$ 10.5, 5-Ha), 3.25 (1H, t, $J_{2,3} = J_{3,4}$ 9.3, 3-H), 3.90 (1H, dd, $J_{4,5b}$ 5.0, $J_{5a,5b}$ 11.4, H-5b), 4.37 (1H, d, $J_{1,2}$ 7.8, 1-H), 5.27, 5.46, 5.52, 5.53 (4H, 4d, *J* 11.4, 11.8, CH_2Ar), 7.93–8.58 (18H, m, Ar); δ_H (400 MHz; DMF-d_7) 2.82 (1H, t, 2-H), 3.00 (1H, ddd, 4-H), 3.29 (1H, t, $J_{4,5b}$ 10.5, 5-Hb), 3.36 (1H, t, $J_{2,3} = J_{3,4}$ 9.5, 3-H), 4.00 (1H, dd, $J_{4,5a}$ 5.2, $J_{5a,5b}$ 11.4 Hz, 5-Ha), 4.48 (1H, d, $J_{1,2}$ 7.8, 1-H), 5.36, 5.62, 5.64, 5.67 (4H, 4d, *J* 11.3, 11.8, CH_2Ar), 8.04–8.72 (18H, m, Ar); δ_C (67.8 MHz; $CDCl_3$; Me_4Si) 52.4 (*C*-4), 57.3 (*C*-2), 68.0 (*C*-5), 69.2 (CH_2Ar), 72.8, 86.6 (*C*-3), 103.6 (C-1), 123.3, 123.3, 124.5, 124.7, 125.0, 125.3, 126.0, 127.1, 127.4, 127.5, 127.6, 127.7, 128.0, 128.0, 129.2, 129.7, 130.2, 130.7, 131.2, 131.4,1131.5, 31.6; HRMS(ESI) Found: 577.2490 $[M + H]^+$. Calc. for $C_{39}H_{33}N_2O_3$: 577.2491.

NMR experiments for addition of metal ions to compound 1

1 (16.3 mM) with 5.0 equiv. $ZnCl_2$: δ_H (400 MHz; acetone-d_6 0.5 mL; 18.8 °C) 3.65 (1H, d, 5-Ha), 4.10 (1H, s, 4-H), 4.19 (1H, s, 2-H), 4.30 (1H, s, 3-H), 4.60 (1H, dd, $J_{4,5b}$ 2.3, $J_{5a,5b}$ 12.2 Hz, 5-Hb), 4.96 (1H, s, 1-H), 5.32 (1H, d, *J* 11.9, CH_2Ar), 5.40 (1H, d, *J* 11.6, CH_2Ar), 5.48 (1H, d, *J* 11.9, CH_2Ar), 5.49 (1H, d, *J* 11.3, CH_2Ar), 7.60–8.28 (18H, m, Ar).

1 (18.03 mM) with 9.8 equiv. $Mg(ClO_4)_2$: δ_H (400 MHz; acetone-d_6 0.5 mL; 20.0 °C) 3.73 (1H, dd, $J_{4,5a}$ 8.7, $J_{5a,5b}$ 11.4, 5-Ha), 4.11 (1H, t, 2-H), 4.19 (1H, dd, $J_{4,5b}$ 3.8, $J_{3,4}$ 9.6, 4-H), 4.24–4.36 (2H, br, 3-H, 5-Hb), 4.89 (1H, d, $J_{1,2}$ 6.7, 1-H), 5.30 (1H, d, *J* 11.9, CH_2Ar), 5.31 (1H, s, CH_2Ar), 7.95–8.31 (18H, m, Ar).

Dichloro-[1-pyrenylmethyl 3-*O*-(1-pyrenylmethyl)-2,4-diamino-2,4-dideoxy-β-D-xylopyranoside-*N*,*N*′]-platinum, 1–Pt. To a solution of **1** (6.5 mg, 22.5 mM) in DMF-d_7 (0.5 mL) was added 1.0 equiv. of $K_2[PtCl_4]$ (4.7 mg). The mixture was at first a suspension and turned into a solution over time. The NMR was measured after 15 h. The solution was concentrated and the residue was washed with methanol–H_2O and $CHCl_3$. The solid was dried under reduced pressure.

1–Pt: mp 250 °C (decomp.); $[\alpha]_D^{28}$ −46.5 (*c* 0.4 in DMF); Found: C, 55.3; H, 3.9; N, 3.6. Calc. for $C_{39}H_{32}Cl_2N_2O_3Pt$: C, 55.6; H, 3.8; N, 3.3%; δ_H (400 MHz; DMF-d_7; 19.5 °C) 2.92 (1H, m, 4-H), 3.20 (1H, s, 2-H), 3.90 (1H, d, 5-Ha), 3.96 (1H, s, 3-H), 4.44 (d, 1H, $J_{5a,5b}$ 12.5, 5-Hb), 5.36 (1H, s, 1-H), 5.27, 5.33, 5.39, 5.55 (1H × 4, d × 4, *J* 11.7, 12.2, CH_2Ar), 7.72–8.51 (18H, m, Ar); δ_C (67.8 MHz; $CDCl_3$) 47.4, 48.0, 57.1, 68.1, 69.9, 75.3, 97.5, 123.8, 124.0, 124.4, 124.5, 124.5, 124.7, 124.8, 125.3, 125.4, 125.5, 126.3, 126.4, 127.2, 127.4, 127.5, 127.7, 127.8, 129.1, 129.4, 130.8, 130.9, 131.1, 131.3, 131.4, 131.9, 132.0.

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