A sugar–pyrene-based fluorescent gelator: nanotubular architecture and interaction with SWCNTs†‡

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Received (in Gainesville, FL, USA) 7th August 2009, Accepted 13th October 2009
First published as an Advance Article on the web 30th October 2009
DOI: 10.1039/b9nj00395a

A sugar–pyrene-based fluorescent gelator was synthesised and characterized based on different spectral techniques. The weak interactions that exist between the pyrene moieties are responsible for gelation, which is absent in case of functionalised SWCNTs.

Molecular self-assembly is becoming a popular tool for constructing different types of micro- and nanostructured materials.[1–4] Low molecular weight organogelators (LMOGs) have a wide range of applications in the field of materials, biology, drug design and natural product chemistry.[5–9] LMOGs are known as distinct soft materials and can self-assemble into various types of fibrils, strands and tapes in organic solvents *via* weak intermolecular interactions.[10] In an organogel medium, one-dimensional (1-D) supramolecular fibers are bundled up together and entangled at nodes, so-called "junction points", to form three-dimensional (3-D) network structures, within which the solvent molecules are entrapped. The nanostructured functional molecular assembly thus created is a promising candidate for organic devices with intriguing photo- and electrochemical functions.[1–3,11] Materials design is a highly competitive area of current research. Many of the reported materials are derived from complicated molecules[9] that are laborious to synthesize and also expensive. Even though many compounds are effective gelators, they don't have suitable functional groups that can bind to other materials, such as nanoparticles. In this context, pyrene-based and functionalized LMOGs are simple compounds that are extremely effective at gelling many organic solvents at less than 1% concentration.[12] However, the pyrene-derived gelators investigated so far possess no functionality other than van der Waals interactions to bind materials into gel networks or to control the gel structure. The interaction of CNTs with gelators and their self-assembly have received a great deal of interest because of their unique structural, electrical and mechanical properties.[13] Highly functionalized nanotubes have been studied widely for potential applications in gene therapy,[14] drug delivery,[15] enzyme immobilization,[16] bio-sensing,[17] heat transfer and thermal management.[18]

Recently, we reported the gelating abilities of different sugar derivatives[10] and also studied the thermal conductivity of sugar-coupled single-walled carbon nanotubes (SWCNTs).[19]

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† Dedicated to Professor C. P. Rao.
‡ Electronic supplementary information (ESI) available: Further experimental data and spectra. See DOI: 10.1039/b9nj00395a

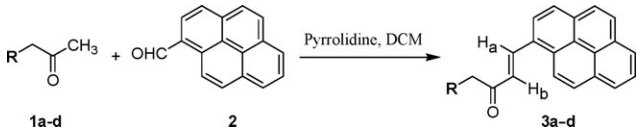
In the present study, we report a novel class of functionalized low molecular weight gelators derived from sugar–pyrene derivatives that have the ability to effectively bind with SWCNTs. The wide range of applications of SWCNTs in the field of materials and biology inspired us to make this further research step in the field.

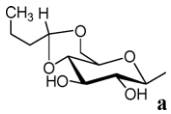
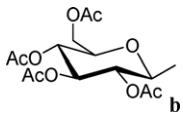
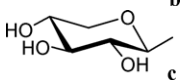
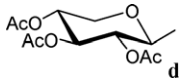
4,6-*O*-Butylidene-D-glucopyranose was synthesized from D-glucose.[20] Various β-*C*-glycosidic ketones were synthesised in good yield by following reported literature procedures.[21,22] The aldol condensation of β-*C*-glycosides **1a–d** with 1-pyrene carboxaldehyde (**2**) was carried out at ambient temperature in the presence of a catalytic amount of pyrrolidine.[10a] Formation of the expected product was confirmed by ^{1}H and ^{13}C NMR spectral studies. The ^{1}H NMR spectrum of α,β-unsaturated-β-*C*-glycosides **3a–d** showed a signal at around 6.5–7.0 ppm for the H_a proton and at around 8.5 ppm for the H_b proton (Table 1).

Among the various sugar-based pyrene derivatives reported in this Letter, (*E*)-1-(4,6-*O*-butylidene-β-D-glucopyranosyl)-4-(1-pyrene)-but-3-en-2-one (**3a**) forms a gel (CGC: 1.0%), prepared by dissolving the gelator in an appropriate amount of DMSO with the further addition of a few drops of H_2O ($DMSO:H_2O$ = 8 : 2). van der Waals interactions exist between the gelator molecules, resulted in a gel network, and these interactions control the gel's structure. In order to understand the involvement of the different groups in the gelation process, we have studied the gelation by variable temperature NMR (VT-NMR) (Fig. 1).

Compound **3a** shows broadening of the signals in both the pyrene and sugar regions due to molecular aggregation. However, a definitive interpretation of such behavior requires careful analysis. In the present case, further evidence for the influence of the association of the pyrene moiety was inferred from the VT-NMR studies. The ^{1}H NMR spectrum of **3a** recorded at RT shows a broadening of the signals. An increase in temperature to 80 °C shows an upfield shift of the pyrene and alkenic protons, the shift being due to pyrene–pyrene interactions. In order to understand more about the role of the sugar in the gelation process, we have synthesised four different sugar–pyrene derivatives. Among these derivatives, **3a** forms a gel due to the presence of the butylidene group, which is responsible for the self assembly. Some of the sugar-based low molecular weight gelators have shown remarkable applications,[1–3] and the gelator reported in this Letter also exhibits a fluorescent nature. This class of sugar–pyrene fluorescent molecule are likely to have a wide range of applications in different fields.

Table 1 Synthesis of sugar-coupled pyrene derivatives **3a–d**



Entry	R(**1/3a–d**)	Time/h	Yield (%)	δ_{H_a}/ppm	δ_{H_b}/ppm	$^3J_{H_a-H_b}$/Hz
1	 **a**	16	80	7.17	—[a]	15.9, —[a]
2	 **b**	10	80	6.93	8.62	15.9, 15.6
3	 **c**	12	72	7.10	8.67	15.9, 15.9
4	 **d**	12	78	6.92	8.60	15.6, 15.6

[a] Peak merged with aromatic protons.

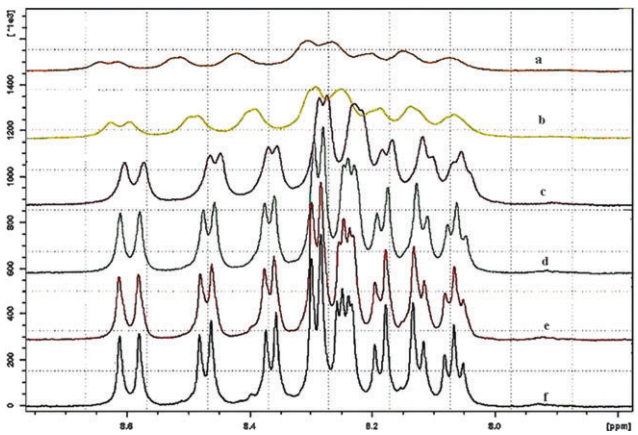


Fig. 1 VT-NMR spectra of compound **3a** in DMSO-d_6 + D_2O at (a) room temperature, and at (b) 40, (c) 50, (d) 60, (e) 70 and (f) 80 °C.

The fluorescent nature of the gel under both visible and UV light is shown in Fig. 2. Sugar-based pyrene derivatives **3a–d** showed characteristic UV absorbance and emission bands (Fig. 3). Upon excitation with 365 nm light, emission bands were observed at 524, 526, 524 and 527 nm for compounds **3a–d**, respectively.

In general at room temperature, SWCNTs have a significantly higher thermal conductivity (6000 W mK^{-1}),[23] and the dispersion of nanotubes in fluid media can lead to a wide range of thermal conductivities, depending upon factors such as volume fraction, method of synthesis, *etc.*[24] One of the specific problems encountered with SWCNTs is their dispersion in fluids. Most SWCNT fluids form clusters, and the efficacy is found to be reduced. Sugar–pyrene-functionalized SWCNTs were synthesised by sonicating a 10 : 1 ratio of compound **3a**

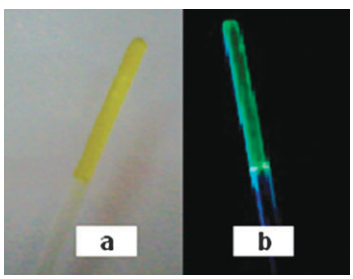


Fig. 2 Gel pictures of compound **3a** in DMSO + D_2O (a) under normal light and (b) fluorescence under UV light.

with SWCNTs,[25] and their dispersion in H_2O was found to be relatively improved. The formation of a dispersed product was confirmed by ^1H NMR, HRSEM and DSC studies. The ^1H NMR spectra of gelator **3a** in the solid phase, gel phase and sugar–pyrene-functionalized SWCNTs are shown in Fig. 4. The ^1H NMR spectrum of functionalized SWCNTs dispersed in D_2O did not show any characteristic peaks, whereas in DMSO-d_6 it showed broadening of the signals, confirming the formation of sugar–pyrene-functionalized SWCNTs. Thus, functionalised SWCNTs were not found to be an efficient gelator due to the absence of the weak interactions that exist between pyrene moieties (Fig. 5).

The self-assembled aggregates of gelator **3a** and functionalized SWCNTs were studied by HRSEM. The purity of the SWCNTs were confirmed by HRTEM analysis (Fig. 6(a) and (b)). Morphological HRSEM images of the functionalized SWCNTs are shown in Fig. 6(c) and (d). HRSEM analysis of gel **3a** shows three modes of aggregation: fibrous, tubular and lamellar. It is interesting to obtain further insight into gelator **3a**, which shows a transparent nanotube-like architecture (Fig. 6(e) and (f)), similar to the recently reported

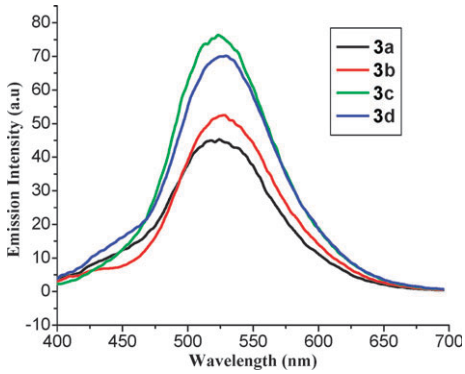


Fig. 3 Emission spectra of compounds (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d** recorded at a 1×10^{-7} M concentration in methanol at 298 K (λ_{exc} = 365 nm).

electroactive nanorod and nanorings formed by the supramolecular association of π-conjugated systems.[26]

To study the thermal properties of gelator **3a** we obtained differential scanning calorimetry (DSC) data (Fig. 7). The melting peak of gelator **3a** was 220.3 °C in the solid phase, with ΔH = 118.6 J g^{-1}, whereas, in the case of the gel phase, several melting peaks were observed at 128.4, 131.3, 132.5 and 135.0 °C, with ΔH = 723.2 J g^{-1}, which may be due to various modes of aggregation (Fig. 7(a)). In order to find the sol–gel transition temperature of **3a**, the gel was heated to 170 °C and allowed for cool to room temperature. During the cooling cycle, two endothermic peaks were observed at 79.9 °C, with ΔH = −1.057 J g^{-1}, and 55.1 °C, with ΔH = −2.457 J g^{-1}, respectively, which could be attributed to the conversion of the sol to the gel (Fig. 7(b)). The melting peak and enthalpy value of functionalized SWCNTs were found to be 219.7 °C and ΔH = 84.6 J g^{-1}, respectively. Neither **3a** nor the functionalized SWCNTs showed any endothermic peaks. Microanalysis of the elements present in the gel and the functionalized SWCNTs were obtained using EDAX (see the ESI for details‡). In order to determine the thermal conductivity of gelator **3a**, the gel and the functionalized SWCNT materials, they were heated at a rate of 10 K min^{-1} and allowed to cool at

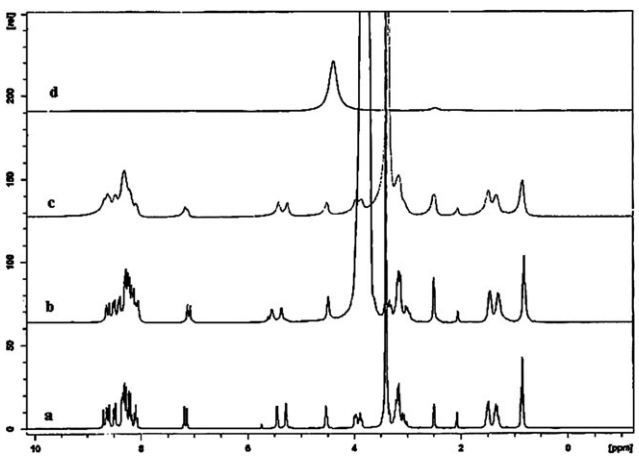


Fig. 4 The ^{1}H NMR spectrum of (a) gelator in DMSO-d_6, (b) gel in DMSO-d_6 with a few drops of D_2O, (c) functionalized SWCNTs in DMSO-d_6 and (d) functionalized SWCNTs in D_2O.

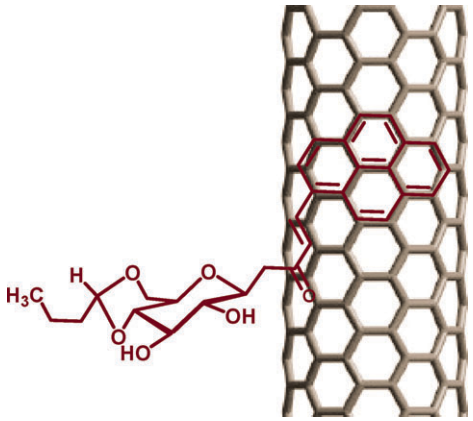


Fig. 5 The interaction of sugar–pyrene derivative **3a** with a SWCNT.

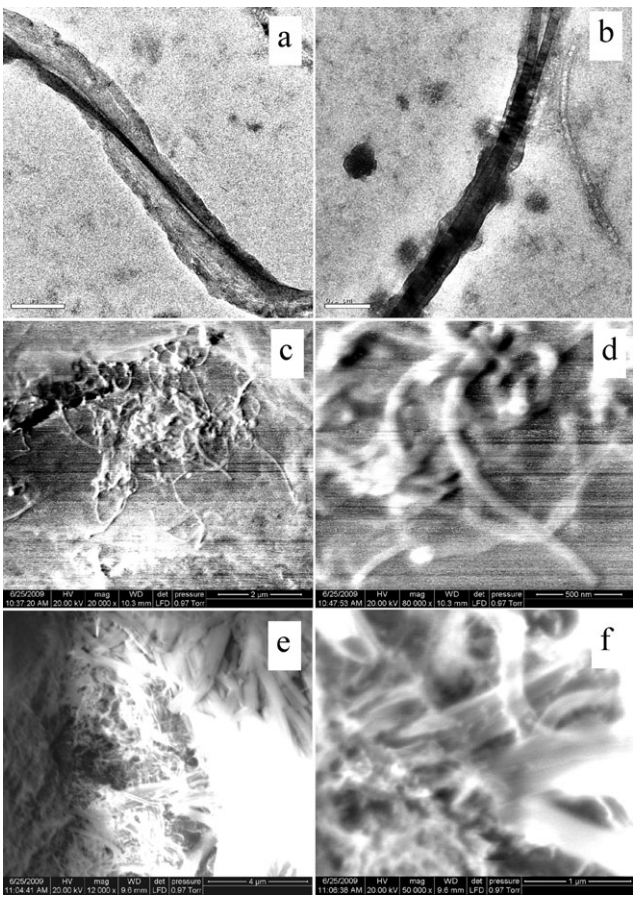


Fig. 6 Morphological images of SWCNTs, functionalized SWCNTs and **3a**: (a) HRTEM image of an SWCNT, (b) HRTEM image of an SWCNT, (c) HRSEM image of functionalized SWCNTs (2 μm), (d) HRSEM image of functionalized SWCNTs (500 nm), (e) HRSEM image of gel **3a** (4 μm) and (f) HRSEM image of gel **3a** (1 μm).

a constant rate using DSC. The cooling time of the gel, the functionalized SWCNTs and gelator **3a** were found to be 5.79, 5.89 and 6.13 s K^{-1}, respectively, and could be attributed to the greater thermal conductivity properties of the nanotubular gel and functionalized SWCNTs than the gelator.

In conclusion, we have investigated the gelation properties of a novel class of sugar–pyrene-based low molecular weight

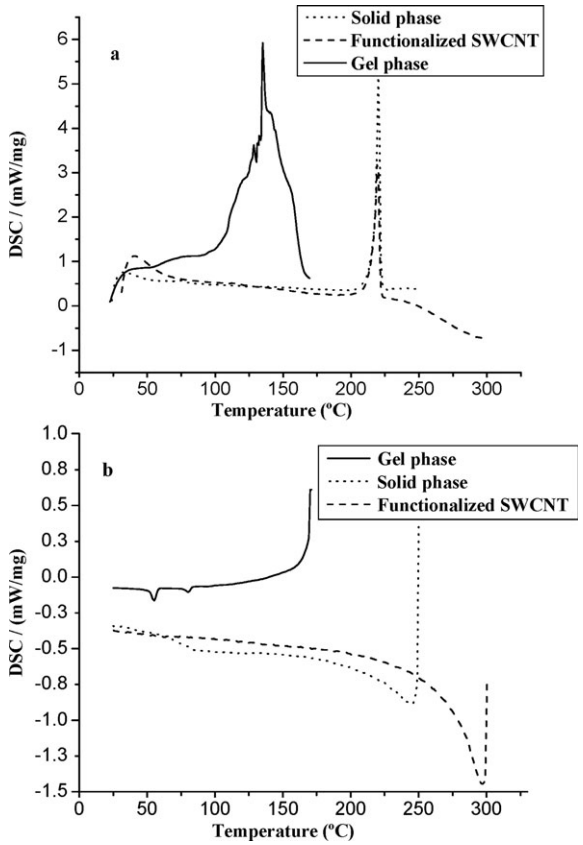


Fig. 7 DSC of the gelator, functionalized SWCNTs and gel: (a) heating curves and (b) cooling curves.

fluorescent gelators. Our studies show that the weak van der Waals interactions that exist between pyrene moieties is largely responsible for gelation. Functionalized SWCNTs did not show gelation properties due to the absence of weak interactions between the pyrene moieties. The interaction of SWCNTs with **3a** had a negative effect on the gelation ability of the molecules. However, DSC studies showed that the functionalised SWCNTs and nanotubular gel had a greater thermal conductivity compared to simple SWCNTs and pyrene-based gelators.

The authors acknowledge UGC and DST, New Delhi, India for financial support. We thank DST, New Delhi for NMR facilities under the DST-FIST scheme to the Department of Organic Chemistry, University of Madras, Chennai, India. T. M. thanks Dr. A. K. Mohanakrishnan, Department of Organic Chemistry, University of Madras, Chennai-25 for fluorescence studies. We also thank Prof. K. A. Padmanabhan, Anna University, Chennai-25 for a SWCNT sample. S. N. thanks UGC, New Delhi for a Research Fellowship.

Experimental

Materials and methods

D-Glucose, D-xylose and 1-pyrene carboxaldehyde, used for the synthesis of the nanomaterials, were obtained from Sigma-Aldrich Chemicals Pvt. Ltd., USA and were of high purity. Butyraldehyde and the organocatalyst (pyrrolidine) were obtained from SRL, India. Other reagents, such as hydrochloric acid, sodium bicarbonate and solvents (AR Grade), were obtained from Sd-fine, India, were of high purity and were used without any further purification. Acetic anhydride was purchased from Fischer Chemcials Pvt. Ltd., India. Column chromatography was performed on silica gel (100–200 mesh). NMR spectra were recorded on a Bruker DRX 300 MHz instrument in either $CDCl_3$, DMSO-d_6 or $CDCl_3$ (with a few drops of DMSO-d_6); chemical shifts were referenced to internal TMS. DSC was undertaken on a Netzsch DSC 204 instrument. Emission spectra were recorded on a Perkin-Elmer LS-45 spectrophotometer. HRSEM images and microanalysis (EDAX) were recorded using a FEI Quanta FEG 200 high resolution scanning electron microscope. Elemental analysis was performed using a Perkin-Elmer 2400 series CHNS/O analyser. For complete characterization of the starting material, HRTEM micrographs were recorded using a Jeol JEM 3010 instrument (LaB6 filament).

Synthesis of sugar–pyrene-functionalized SWCNTs. 10 mg of SWCNTs were dispersed in 15 ml of distilled H_2O containing 100 mg of gelator **3a**. The mixture was sonicated for about 1 h, after which it was centrifuged at 5000 rpm and the centrifugate subsequently decanted. In order to remove the free sugar–pyrene derivative, the residue was washed several times (3–4 times) with methanol. The sugar–pyrene-functionalized SWCNTs thus obtained were dried and used for further studies.

General procedure for the synthesis of (*E*)-1-sugar-substituted-4-(1-pyrene)-but-3-en-2-ones. To a solution of β-*C*-glycosidic ketone (1 mmol) in dry DCM was added pyrrolidine (30% mol) and **2** (1.2 mmol). After stirring at room temperature for given period of time, the reaction mixture was evaporated under reduced pressure and extracted with EtOAc–H_2O. The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated to dryness. The product was further purified by flash column chromatography.

Synthesis of (*E*)-1-(4,6-*O*-butylidene-β-D-glucopyranosyl)-4-(1-pyrene)-but-3-en-2-one (3a). Compound **3a** was obtained by the reaction of β-*C*-glycosidic ketone **1a** (1 mmol, 0.274 g) and **2** (1.2 mmol, 0.276 g) as a yellow solid: mp 217–219 °C. Yield: 0.390 g (80%). ^{1}H NMR (300 MHz, TMS/ppm): 8.62 (t, J = 8.7 Hz, 1H), 8.49 (d, J = 8.1 Hz, 1H), 8.26–8.36 (m, 5H), 8.20 (t, J = 8.7 Hz, 2H), 8.10 (t, 1H), 7.17 (d, J = 15.9 Hz, 1H), 5.45 (d, J = 5.7 Hz, 1H), 5.29 (d, J = 4.8 Hz, 1H), 4.54 (s, 1H), 3.96–3.99 (dd, J = 3.6 Hz, J = 4.2 Hz, 1H), 3.89 (t, J = 8.1 Hz, 1H), 3.04–3.49 (m, 7H), 1.47–1.52 (m, 2H), 1.31–1.38 (m, 2H) and 0.85 (t, 3H). ^{13}C NMR (75 MHz, TMS/ppm): 197.8, 138.4, 130.8, 130.2, 129.4, 129.1, 128.6, 128.1, 127.3, 126.6, 126.1, 125.9, 125.3, 124.5, 124.0, 123.7, 122.5, 101.3, 80.7, 77.0, 74.3, 74.1, 70.3, 67.5, 43.3, 35.8, 17.2 and 13.9. Elemental analysis found: C, 74.20; H, 6.04. Calc. for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21%.

Synthesis of (*E*)-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(1-pyrene)-but-3-en-2-one (3b). Compound **3b** was obtained by the reaction of β-*C*-glycosidic ketone **1b** (1 mmol, 0.388 g) and **2** (1.2 mmol, 0.276 g) as a yellow solid: mp 170–172 °C.

Yield: 0.480 g (80%). ^{1}H NMR (300 MHz, TMS/ppm): 8.62 (d, J = 15.6 Hz, 1H), 8.35 (d, J = 9.3 Hz, 1H), 8.09–8.19 (m, 3H), 8.02–8.07 (m, 3H), 7.92–7.97 (m, 2H), 6.93 (d, J = 15.9 Hz, 1H), 5.21 (t, 1H), 4.97–5.09 (m, 2H), 4.14–4.25 (m, 2H), 3.98–4.02 (dd, J = 2.1 Hz, J = 12.6 Hz, 1H), 3.67–3.73 (m, 1H), 3.04–3.12 (q, J = 8.4 Hz, 1H), 2.73–2.78 (dd, J = 3.3 Hz, J = 16.5 Hz, 1H) and 1.90–1.96 (m, 12H). ^{13}C NMR (75 MHz, TMS/ppm): 196.0, 170.6, 170.3, 170.0, 169.6, 140.2, 133.1, 131.3, 130.6, 130.3, 128.9, 128.8, 127.8, 127.3, 126.4, 126.2, 126.0, 125.1, 124.9, 124.5, 124.1, 122.2, 75.9, 74.4, 74.3, 71.8, 68.6, 62.1, 43.2 and 20.7. Elemental analysis found: C, 67.75; H, 5.25. Calc. for $C_{34}H_{32}O_{10}$: C, 67.99; H, 5.37%.

Synthesis of (*E*)-1-(β-D-xylopyranosyl)-4-(1-pyrene)-but-3-en-2-one (3c). Compound **3c** was obtained by the reaction of β-*C*-glycosidic ketone **1c** (1 mmol, 0.274 g) and **2** (1.2 mmol, 0.276 g) as a yellow solid: mp 132–134 °C. Yield: 0.290 g (72%). ^{1}H NMR (300 MHz, TMS/ppm): 8.67 (d, J = 15.9 Hz, 1H), 8.48 (d, J = 9.6 Hz, 1H), 8.36 (d, J = 8.1 Hz, 1H), 8.25 (d, J = 7.5 Hz, 2H), 8.03–8.19 (m, 5H), 7.10 (d, J = 15.9 Hz, 1H), 3.68–3.76 (m, 2H), 3.45–3.48 (m, 1H), 2.93–3.33 (m, 5H), 2.78–2.90 (m, 1H) and 2.40–2.77 (m, 1H). ^{13}C NMR (75 MHz, TMS/ppm): 198.0, 138.2, 132.0, 130.7, 130.1, 129.3, 128.8, 128.4, 127.9, 127.1, 126.3, 125.9, 125.6, 125.0, 124.1, 124.0, 123.7, 122.2, 78.1, 77.2, 76.7, 73.5, 69.9, 69.7, 46.2 and 30.2. Elemental analysis found: C, 74.88; H, 5.76. Calc. for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51%.

Synthesis of (*E*)-1-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-4-(1-pyrene)-but-3-en-2-one (3d). Compound **3d** was obtained by the reaction of β-*C*-glycosidic ketone **1d** (1 mmol, 0.316 g) and **2** (1.2 mmol, 0.276 g) as a yellow syrup. Yield: 0.410 g (78%). ^{1}H NMR (300 MHz, TMS/ppm): 8.60 (d, J = 15.6 Hz, 1H), 8.32 (d, J = 9.0 Hz, 1H), 7.99–8.16 (m, 4H), 7.05–7.95 (m, 4H), 6.92 (d, J = 15.6 Hz, 1H), 5.19 (d, J = 9.3 Hz, 1H), 5.10 (d, J = 9.6 Hz, 1H), 4.87–4.97 (m, 1H), 3.93–4.07 (m, 2H), 3.30 (d, J = 10.8 Hz, 1H), 3.19 (d, J = 10.8 Hz, 1H), 3.01 (d, J = 8.4 Hz, 1H), 2.69–2.75 (m, 1H) and 1.91–1.98 (m, 9H). ^{13}C NMR (75 MHz, TMS/ppm): 196.3, 170.3, 170.1, 169.9, 140.3, 133.0, 131.2, 130.1, 128.8, 127.8, 127.3, 126.3, 126.2, 126.0, 125.0, 124.9, 124.5, 124.1, 122.2, 75.0, 73.8, 72.0, 69.3, 66.8, 45.4, 43.2, 31.1 and 20.7. Elemental analysis found: C, 70.21; H, 5.60. Calc. for $C_{31}H_{28}O_8$: C, 70.44; H, 5.34%.

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