Rigid rod and tetrahedral hybrid compounds featuring nucleobase and nucleoside end-capped structures†

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Being aimed at a new type of porous solids, a moduled design strategy of molecular tectons, making use of the conjugation between a shape defined artificial backbone and the bioinspired molecular fragments of nucleobases or nucleobase derivatives as functional end-caps, has been developed. This led to the formation of the new hybrid compounds **1–13** of linear and tetrahedral geometry, containing uracil, adenine, adenosine, guanosine and its acylated analogs as the sticky end-cap sites. The compounds were synthesized from a halogen or ethynyl substituted nucleobase component and the corresponding ethynylated spacer unit following a metal assisted coupling process as the key reaction step. X-Ray crystal structure analysis demonstrates that the parent compound **1** is a solvent complex with DMSO (1:2), showing the DMSO molecules incorporated in a hydrogen bonded layer structure. Specific dependencies of the fluorescence properties of the new compounds in solution on the structure of the molecules are reported. A selection of solid compounds has been studied in respect of their ability to adsorb organic vapours. They revealed significant differences both in the sorption capacity and the selectivity towards particular solvent vapours.

Introduction

The conjugation of moduled synthetic building blocks to introduce parameters of a specific shape or functionality with components to interface efficiently with biological systems is a highly challenging topic.[1] Hybrid compounds emerging from this are promising targets in many significant fields including molecular diagnostics,[2] tissue engineering,[3] manipulation of cell adhesion[4] and other tools for chemical biology.[5] Moreover, they are also expected to be useful in the development of chemical sensors[6] and adsorbents[7] or potentially for the construction of future electronic and optical devices.[8]

Important examples of structural units of high biological relevance are nucleobases,[9] which possess a crucial factor for the stability of nucleic acid duplexes and logically are a vital point in the very essential fields of genetic coding, biological information storage and protein biosynthesis.[10] Therefore, nucleobase derivatives are widely used for medicinal or genetic applications.[11] On the other hand, considering their general importance, the potential of nucleobases as tools in supramolecular chemistry has not yet been fully exhausted,[12] although they have been rather broadly studied and currently reviewed in this respect by the groups of Sessler[13] and Rowan.[14] They show the number of different ways that the nucleobases have already been used, including various dimeric and polymeric assemblies, cage construction, metal coordination and other kinds of host–guest or energy transfer systems, mainly based on hydrogen bonding. However, while these interactions were investigated in detail mostly in solution, their use in the formation of new solid materials following the concepts of crystal engineering[15] in order to create porous hydrogen bonds[16] or metal coordination (MOF)[17] crystalline network structures has only scarcely been exploited.[14] This is a noteworthy fact since nucleobases make possible the creation of a quasi model type of supramolecular synthons[18] due to their complementary multiple hydrogen bonding donor and acceptor sites.[13,14] Moreover, nucleobases possessing suitable shapes and systems of π-electrons are also inclined to supramolecular stacking motifs.[19] Both these properties give rise to highly controlled molecular recognition between two matching nucleobases, which would be a special merit of an intended crystalline tecton[20] for a particular solid state construction, similar to the oligotopic 2-pyridinones designed by Wuest[21] or the melamine and barbituric acid complexes of the Whitesides group.[22] A conceptual outline of the intended new type of porous solid structure is illustrated in Fig. 1.

This has stimulated the synthesis of a series of linear and tetrahedral hybrid compounds composed of artificial shape controlling central units and bioinspired sticky terminal groups consisting of a nucleobase or a derivative of it. We report the preparation of these compounds, discuss the crystal structure of a solvated prototype compound, give information on the fluorescence in solution, and describe the sorption behaviour of selected solid materials of this type towards vapours of organic solvents in view of a potential sensor aspect.

Results and discussion

Design strategy of compound structures

In order to obtain compounds featuring the desired property of crystal tectones[20] that will make use of the particular hydrogen

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† Electronic supplementary information (ESI) available: A. Experimental details of compounds **2**, **3**, and **5–14**; B. Spectroscopic data; C. ^{1}H NMR spectra of selected key compounds corresponding to the different structural types; D. Data of non-covalent interactions from the crystal structure analysis. CCDC reference number 722856. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b904889h

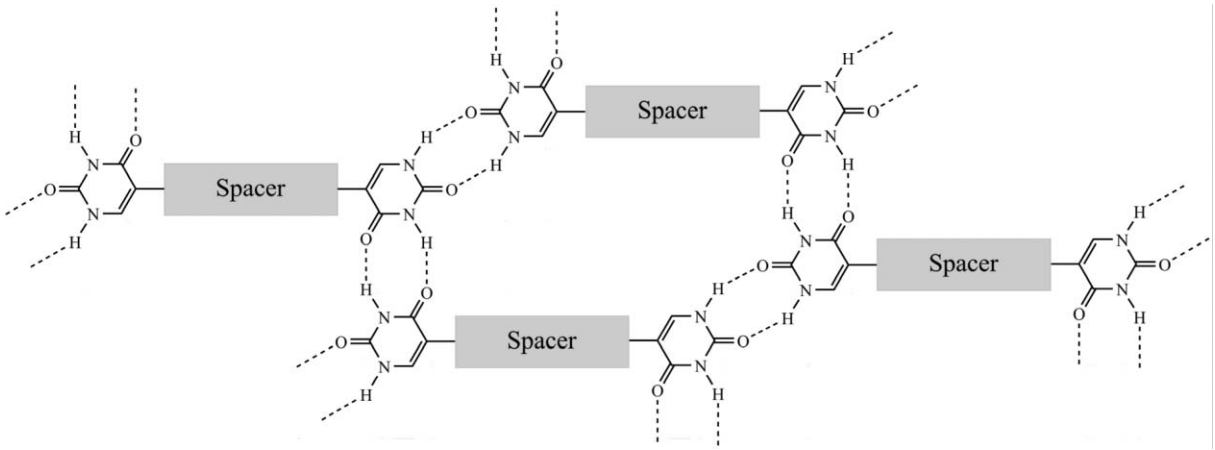

Fig. 1 Conceptual diagram illustrating the intended new porous solid state structures based on a nucleobase pairing of molecular tectons. Two-dimensional sketch by means of an uracil end-capped spacer molecule.

bond and heteroaromatic stacking behaviour of the biological nucleobases, and thus create porous solids (cf. Fig. 1),[13,14] terminal attachment of the respective nucleobases to a shape defined backbone unit should be a promising working plan, as sketched out with the linear and tetrahedral basic structures in Fig. 2. The shape-persistency of the core units (S) is ensured by the use of particularly rigid and strictly geometrical defined aromatic and ethynylene spacer moieties[23] as well as a tetrakis(4-ethynylphenyl)methane building block[24] in the one- and three-dimensional case, given by the linear (I) and tetrahedral (II) structural elements, respectively. The effective distance of the spacer moieties depends on the number of the linear connector units being inserted into the backbone structure. Selected nucleobases or nucleobase derivatives (Nu) applying to Fig. 2 are uracil, adenine, adenosine, and guanosine as well as acetyl and isobutanoyl substituted analogs of the guanosine, respectively. This gives rise to a modular construction principle as shown with the formulas in Fig. 3–5.

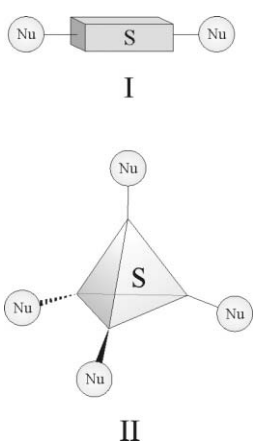

Fig. 2 Structural design concept of the linear (I) and tetrahedral (II) target compounds with *S* referring to the rigid spacer units and *Nu* to the nucleobase and nucleobase derivative terminal components.

Considering the specification listed in Table 1, a subdivision of the compounds **1–13** can be made according to the following scheme: prototype molecule (**1**), linear (**2–8**) and tetrahedral species (**9–13**). The compound **8** represents a special case in that the molecular structure is asymmetric, because it contains a different nucleobase and nucleoside residue at both ends of the linear spacer unit. The nucleoside and substituted nucleoside structures, being present in several of the compounds (**3**, **5–8** and **10–13**), not only serve the purpose of avoiding low solubility of the pure nucleobases and make their synthesis easier,[13,25] but may also promote the polar interactions.

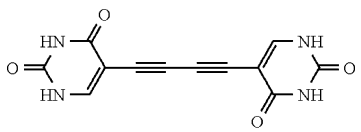

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Fig. 3 Constitutional structure of the linear prototype compound **1**.

Synthesis

The synthesis of the target compounds was performed by metal assisted couplings including Eglinton[26] and Sonogashira–Hagihara[27] procedures as the key reaction steps. These couplings

Table 1 Specification of the linear (arylene-ethynylene spacer type) compounds in this study

Compound	S	Nu	R (R^1-R^3)	R′
2a	A	2 X	—	—
2b	B	2 X	—	—
2c	C	2 X	—	—
3a	A	2 Y	R^1	—
3b	B	2 Y	R^1	—
3c	C	2 Y	R^1	—
4	A	2 Y	H	—
5a	A	2 Z	R^1	H
5b	B	2 Z	R^1	H
5c	C	2 Z	R^1	H
6a	A	2 Z	R^2	H
6b	B	2 Z	R^2	H
6c	C	2 Z	R^2	H
7a	A	2 Z	R^3	*i*-butanoyl
7b	B	2 Z	R^3	*i*-butanoyl
7c	C	2 Z	R^3	*i*-butanoyl
8	A	X, Y	R^1	—

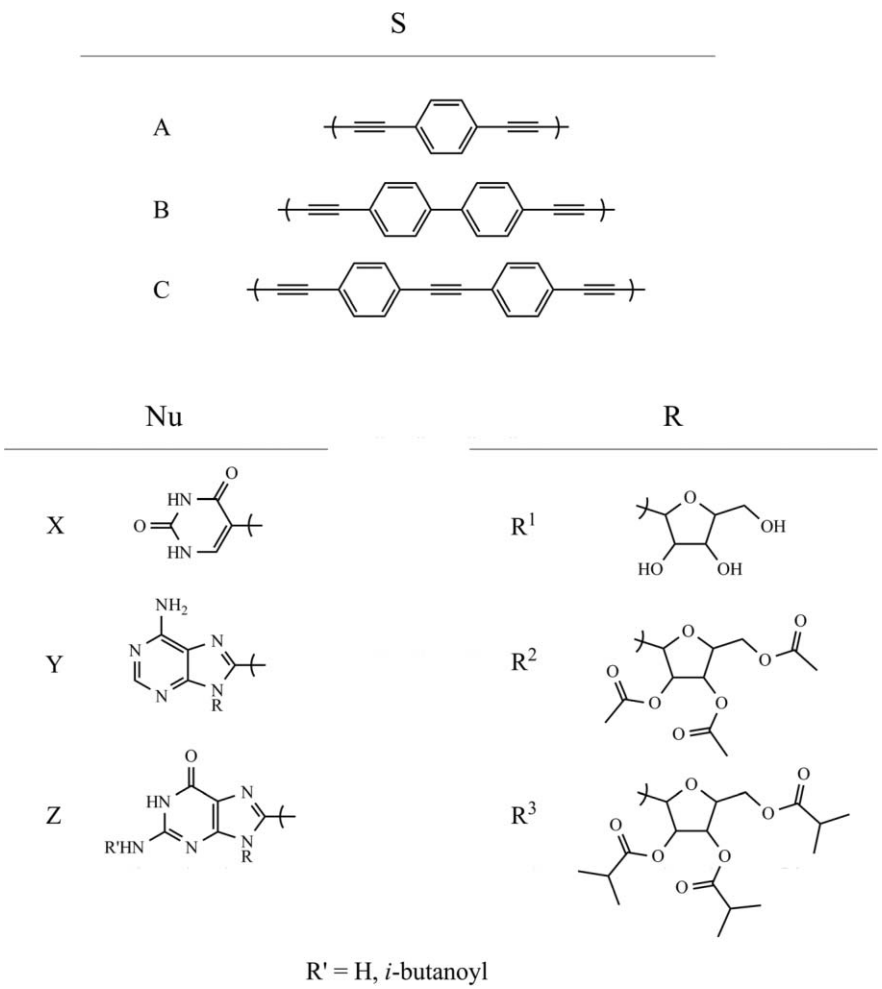


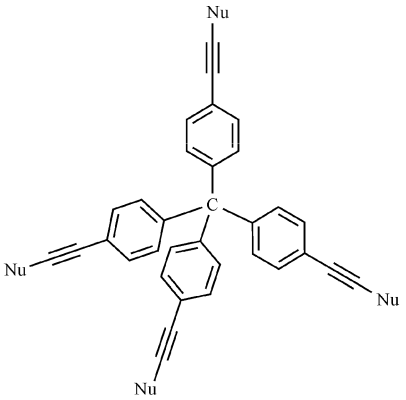
Fig. 4 Linear spacer (A–C), nucleobase and nucleobase derivative (X–Z) constructional components relating to the compound structures of **2–8** (Table 1).

involve reactions between halogen and ethynyl substituted nucleobases or derivatives of nucleobases and ethynylated spacer units. The halogenated nucleobases or nucleobase derivatives that were used for couplings are 5-iodouracil,[28] 8-bromoadenosine,[29] 8-bromoguanosine,[30] 8-bromo-2′3′5′-tri-*O*-acetylguanosine[31] and 8-bromo-2-*i*-butyramido-9-(2′3′5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-6-one.[32] These particular compounds were obtained by halogenation reactions of the corresponding nucleobase or nucleobase derivatives according to literature methods (see Experimental). 5-Ethynyluracil, which is the coupling component for the synthesis of **1**, was prepared from 5-iodouracil and monoprotected trimethylsilylacetylene (TMSA) using the standard Sonogashira–Hagihara conditions, followed by the cleavage of the protecting group, as described.[28]

The linear diethynyl spacer compounds, serving as building blocks for **2–8**, were synthesized from the respective dibromoarene and 2-methyl-3-butyn-2-ol (MEBYNOL)[33] *via* the Sonogashira–Hagihara method[27] and subsequent deprotection of the ethynyl groups[34] (Fig. 6). Tetrakis(4-ethynylphenyl)methane, from which the compounds **9–13** derive, was analogously prepared from tetrakis(4-bromophenyl)methane[35] and MEBYNOL followed by deprotection. It is worth mentioning here that two of these compounds, namely 4,4′-diethynylbiphenyl[36] and tetrakis(4-ethynylphenyl)methane,[37] have previously been synthesized applying the TMSA route which, however, is much more costly compared to the presently used MEBYNOL method. Thus following the latter procedure is the better way to make these compounds accessible.

Examples of synthesis for **1** and **2a** as representatives of the rod-shaped type of compounds (**1–3** and **5–7**), including both the Eglinton[26] and Sonogashira–Hagihara[27] approach of coupling reaction, are illustrated in Fig. 7 and 8, respectively. An analogous coupling under Sonogashira–Hagihara conditions between tetrakis(4-ethynylphenyl)methane and the respective brominated nucleobase derivative was used for the preparation of the tetrahedral compounds **9–13**.

Courses different from those taken above are required for the synthesis of compounds **4** and **8**. While the diadenine **4** was obtained by acid hydrolysis of the nucleoside **3a**, the compound **8** being endowed with different nucleobase derivatives at both ends of the molecule, *i.e.* uracil and adenosine, involves the asymmetrically TMS protected 1,4-diethynylbenzene as one of the starting compounds. This was reacted with 5-iodouracil to yield the monoprotected spacer substituted uracil **14**. Cleavage of the blocking group to give **15** and coupling with 8-bromoadenosine completes the sequence of reactions (Fig. 9).



Compound	Nu	R (R^1-R^3)	R'
9	4 X	—	—
10	4 Y	R^1	—
11	4 Z	R^1	H
12	4 Z	R^2	H
13	4 Z	R^3	*i*-butanoyl

Fig. 5 Basic structure and specification of the tetrahedral compounds (formula assignments in Fig. 3).

All Pd-catalyzed couplings were carried out under argon in DMF or toluene under different conditions of temperature and reaction time, and use of $[Pd(PPh_3)_4]/CuI/Et_3N$ (I)[38] or $[Pd(PPh_3)_2]Cl_2/CuI/Et_3N$ (II)[39] as catalytic systems, depending on the individual case. For instance, the couplings involving 5-iodouracil (**2a–c**, **9** and **14**) were performed in DMF at room temperature with catalyst I, while most of the adenosine containing compounds **3a–c** and **10** were prepared at a higher temperature (110 °C) due to the reduced reactivity of the bromo derivative of adenosine[40] and with the use of catalyst II, except **8** (50 °C, catalyst I, 11 h). The guanosine type compounds **5a–c** and **11** as well as **6a–c** and **12** were coupled in DMF at 70 °C with catalyst I. On the other hand, owing to the increased solubility caused by the *i*-butanoyl groups, the couplings to the compounds

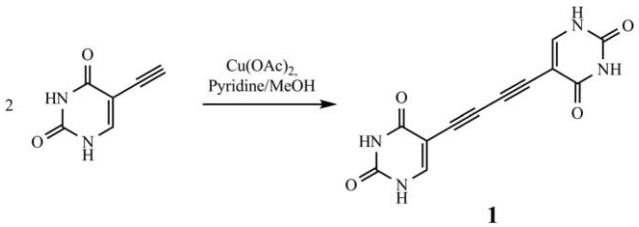


Fig. 7 Synthesis of compound **1** *via* Eglinton coupling.

7a–c and **13** could be carried out with catalyst I in toluene at moderate temperature (50 °C). While in the synthesis of the target compound **1** the Eglinton coupling step gave rise to only a moderate yield of 26%, the coupling reactions according to the Sonogashira–Hagihara method led to much higher yields. Excepting the asymmetrical target compound **8** (final coupling step of 27%), these yields range from about 50% in one case to more than 90% both for the linear (**2–7**, including **14**) and tetrahedral species (**9–13**). All the final product compounds were obtained as powdery solids that show high melting points (>300 °C) or decompose before melting, except the acylated guanosines. They possess lower melting points, decreasing in degrees from acetyl to isobutanoyl groups. Most of the compounds are of low solubility in common organic solvents, making purification processes difficult, excepting the *i*-butanoyl modified guanosines (**7a–c**) which offer the advantage of purification by column chromatography.

In the IR (KBr) spectra, the compounds containing an asymmetrically substituted acetylenic group are typical of an intensive absorption band between 2100–2250 cm^{-1}, as contrasted with the symmetrical ethynes showing only a very weak absorption. A special structural feature is indicative of the pyrimidine ring in compound **15**, being in the tautomeric form of a 2-hydroxy-4-oxopyrimidine structure instead of the commonly observed double lactame structure. This is proven by ^1H NMR (in DMSO-d_6), showing separate signals for the NH (δ = 9.56 ppm) and OH (δ = 4.23 ppm) groups, and is also in correspondence with literature data.[41] Coupling of the halogenated nucleobases with the ethynylated spacer units, making up the key reaction step, led to distinct low field shifts in the ^{13}C NMR spectra with reference to the signals for the C5-pyrimidine and C8-purine carbon atoms, ranging from 25 to 30 ppm for the uracil, and from 5 to 10 ppm for the adenosine and guanosine derivatives. The difference in the strength of the shift between the pyrimidines and the purines is likely to be caused by both the different heterocyles and the different halogens, that is iodine and bromine, which have been

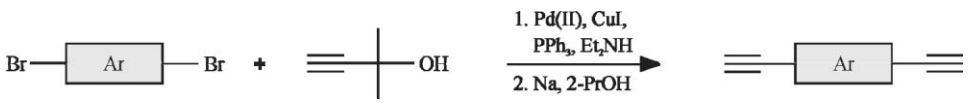


Fig. 6 Synthesis of the linear diethynyl spacer compounds (schematic representation).

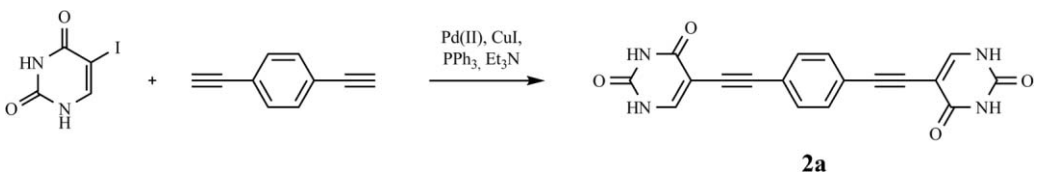


Fig. 8 Synthesis of **2a** *via* Sonogashira–Hagihara coupling.

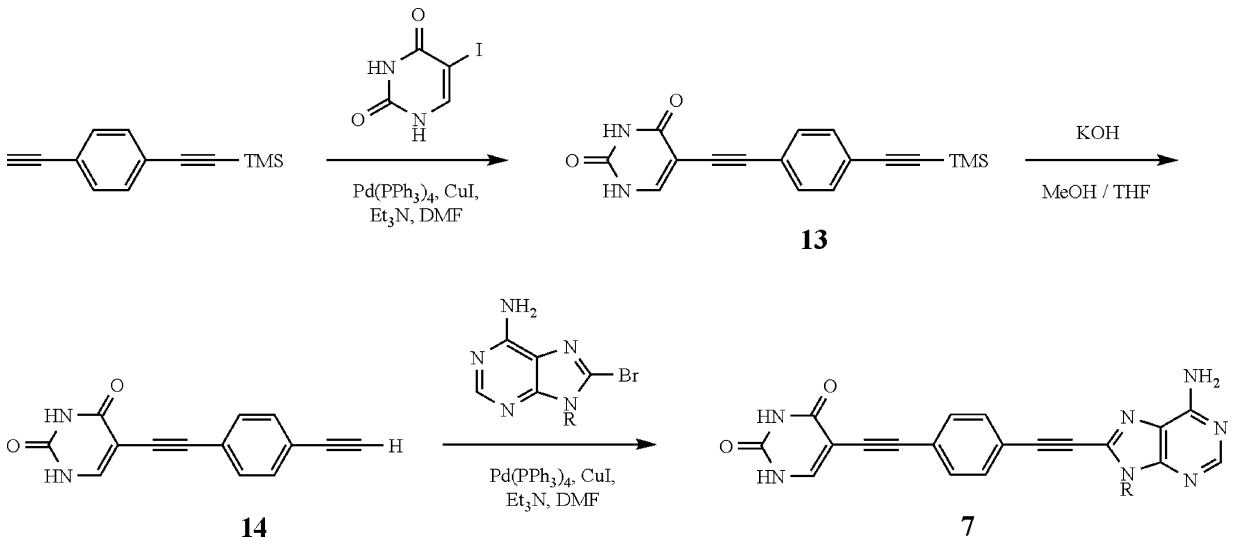


Fig. 9 Synthesis of the asymmetrically end-capped compound **8** (R = R[1], Fig. 4).

used for the halogenated pyrimidines and purines, respectively. However, these shifts may serve as a convenient indication to follow the course of the coupling reactions.

Crystal structure analysis

Due to the low solubility of the nucleobase end-capped compounds in common low or moderate polar organic solvents, the achievement of crystals that can be used for structural analysis is hampered. Obviously, these solvents cannot compete with the strong hydrogen bonds between the end-cap units. Hence, owing to their high effectiveness as hydrogen bond acceptors, DMF and DMSO are expected to be more promising solvents in this respect.[42] However, even when making use of these solvents, only the linear prototype compound **1** was successful in the formation of crystals suitable for an X-ray structural analysis.† They were obtained by slow evaporation of a solution of **1** in DMSO and crystallized in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of **1** and two solvent molecules (Fig. 10), thus being a solvated 1:2 complex of **1** with DMSO.

Due to the planar geometry of compound **1**, the crystal structure is characterized by a sheet-like alignment of molecules which is illustrated in Fig. 11. The packing shows an ABAB-sequence of molecular layers, which are in parallel orientation to the [101]-plane. Within one crystallographic layer, **1** and the solvent molecules form a network stabilized by inverse bifurcated N–H···O hydrogen bonds involving two pyrimidine moieties and a DMSO molecule [d(N1···O5) = 2.808 Å, d(N2···O5) = 2.871 Å and d(N3···O6) = 2.768 Å, d(N4···O6) = 2.843 Å]. Even though the ratio of hydrogen donor (N–H) and acceptor sites (C=O) seems to be balanced for the molecule **1**, no conventional intramolecular hydrogen bonds between two pyrimidine moieties are present; only weak C–H···O and C–H···π-interactions[43,44] can be observed (ESI D†). Hence, the strong hydrogen bond capacity of the nucleobase end-caps is eliminated by the interaction with the solvent molecules.

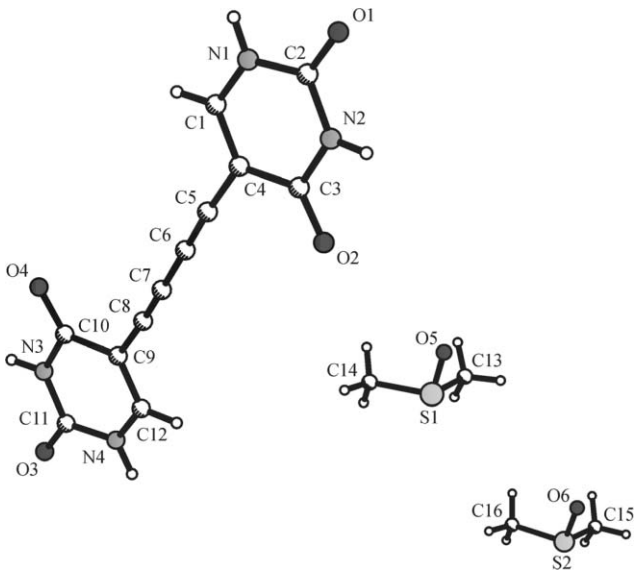


Fig. 10 Molecular structure of **1**·DMSO (1:2), including numbering of non-hydrogen atoms.

Fluorescence properties

Excepting the non-aromatic parent compound **1**, all synthesized nucleobase derivatives containing an aromatic spacer unit are highly fluorescent in solution. Hence, detailed fluorescence measurements were carried out in order to find a potential correlation between molecular constitution and the particular fluorescence maximum. As illustrated with Fig. 12(a–e), the following findings are obvious.

Considering a distinction of the rigid core unit, no clear tendency with reference to the emission maximum or intensity is observed, apart from the fact that tetraphenylmethane derivatives, due to the interrupted electronic conjugation by the central carbon atom, show lower emission maxima than corresponding benzene, biphenyl and tolane species. A comparison of compounds having an identical spacer unit (*e.g.* benzene) but differ in the

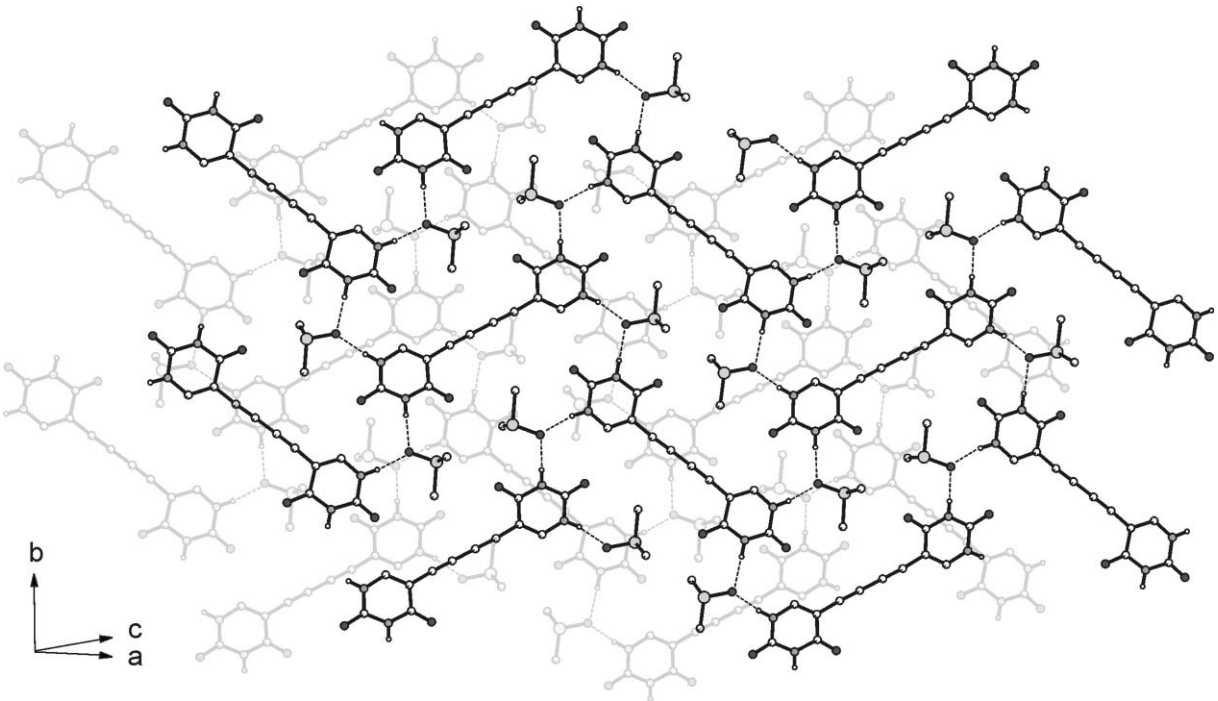


Fig. 11 Packing illustration of **1**·DMSO (1:2), showing the supramolecular layer structure with hydrogen bond interactions given as broken lines (top view). Consecutive layers are specified in bold and light drawing.

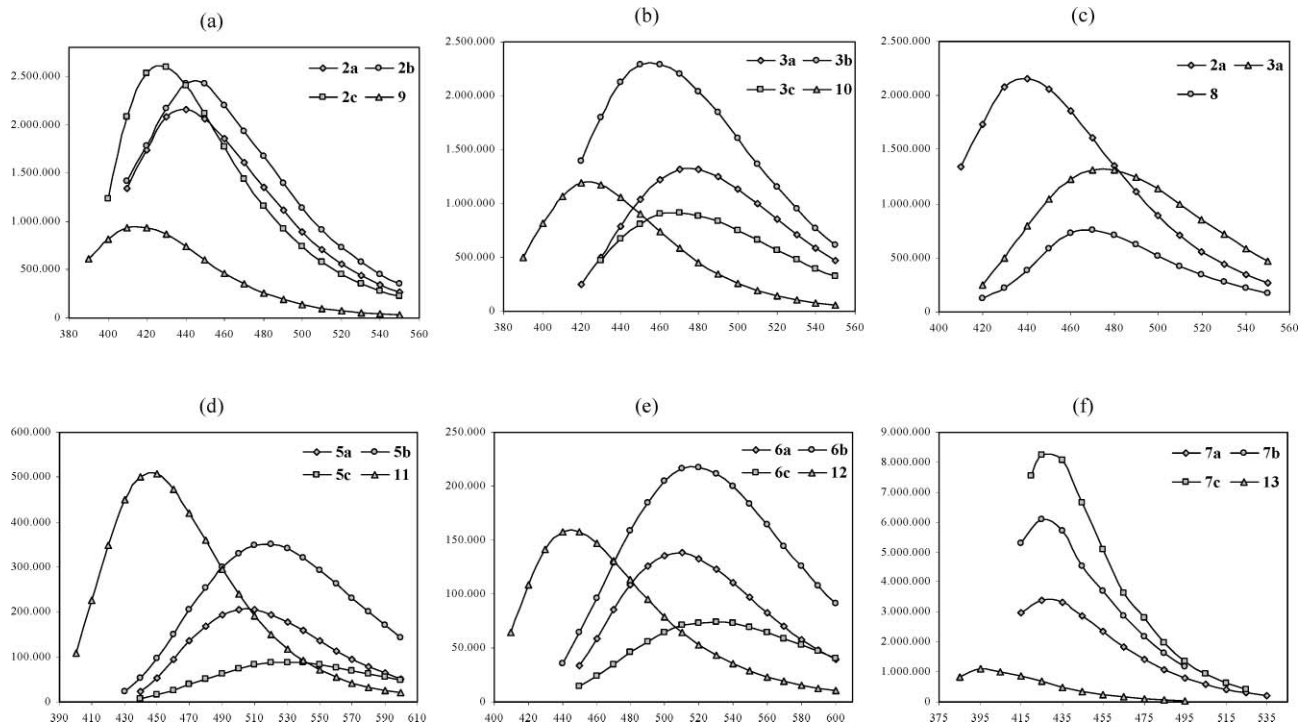


Fig. 12 Fluorescence spectra (0.1 mM solutions of **2**, **3**, **5**, **6**, **8–12** in DMSO and **7**, **13** in $CHCl_3$); intensity (ordinate) against wavelength in nm (abscissa). The individual diagrams relate to derivatives of (a) uracil, (b) adenosine, (c) uracil and adenosine, (d) guanosine, (e) acetyl-protected guanosine, and (f) *i*-butanoyl-protected guanosine.

nucleobase end-caps demonstrates a further noteworthy result. The emission maxima of uracil derivatives are always lower than the maxima of adenosine and guanosine derivatives, with the latter showing the highest values for emission, on principle. On the other side, the unprotected and acetyl-protected guanosine derivatives do not differ significantly in the location of their emission maxima, whereas the *i*-butanoyl-protected derivatives show emission maxima at lower wavelengths and with higher intensities. In conformity with the above observation, the emission maximum of compound **8**, featuring an aromatic spacer unit

with attached uracil and adenosine moieties, lies in between the corresponding values of the maxima of compounds **2a** (uracil) and **3a** (adenosine). In the last analysis, nucleobase moieties as the end-caps connected to a rigid aromatic core unit give rise to a new structural type of luminescent molecules with fluorescent property controllable by the used building blocks.

The receptor and fluorescence properties that meet in the present compounds are rather promising for practical fields of application such as biomarkers in the chemical biology of nucleic acids or a particular segment of DNA.[2,45] Hence, in a first simple test, complementary nucleobases and nucleobase derivatives (adenine, uracil, acetyl-protected cytidin) were added to solutions of the selected compounds **2**, **3** and **6**, respectively. Unfortunately, as yet, in no case of this preliminary study was a usable change of the emission maximum or the intensity detected.

Organic vapour sorption

Although from the BET surface areas[46] that have been taken for random samples of solid compounds **2a**, **2c**, **3c**, **6a**–**6c**, **9**, **10** and **12**, sorption properties of this new type of molecular solids for organic vapours are not very promising, the successful isolation of a crystalline inclusion compound of **1** with DMSO may open potential prospects. These possible expectations are also supported by previous findings mentioned in the literature showing that permanent porosity is not an absolute requirement for the sorptive capability of a molecular solid.[47] Hence a selection of solids of the present new type of compounds was investigated with reference to their potential property of organic vapour sorption. They involve the compounds **2a**, **3a**, **7a**, **10** and **13** being cases in point of linear and tetrahedral compound structures or nucleoside and acylated nucleoside species. The organic vapours that have been selected for the sorption study include compounds such as ethanol, acetone, dichloromethane, tetrahydrofuran and *n*-hexane, being exemplary solvents of high and low polarity as well as of a protic and aprotic nature. A quartz micro balance device[48] was used to determine the sorptive property of the particular solids towards the respective solvent vapours. The results obtained are as follows (Fig. 13).

From among the solvent vapours, dichloromethane is adsorbed the most intensively by all the solids while the adsorption of *n*-hexane is of no significance. Regarding the different solid compounds, the guanosine derivatives **7a** and **13** are the most effective ones both in the capacity and selectivity of sorption featuring a distinct selectivity towards dichloromethane, compared to the adenosine and uracil compounds. On the other hand, these latter compounds show ratios of the adsorbed vapours that are roughly in the same order of magnitude. A comparison of the compounds containing linear and tetrahedral spacer units reveals no significant differences in the guanosine cases (**7a** and **13**), unlike the corresponding adenosines (**3a** and **10**) which are rather different in the sorption of THF, with the tetrahedral derivative **10** being superior. Another remarkable finding is shown by the adenosine compounds **3a** and **10** providing a rather strongly developed sorption of ethanol, in contrast to the acylated guanosines, suggesting the potential ability of the adenosine hydroxy groups to contact to the ethanol molecule *via* hydrogen bonding. The linear uracil derivative **2a** behaves as the less efficient adsorbent in the series of the molecular solids, possibly indicating the high stability of the packing structure, whereas the crystalline frameworks formed of the bulkily substituted guanosine and adenosine molecules are more open to the vapour attack. Basically, for the studied solids, it would seem that the property of organic vapour sorption shows some correlation between the polarity of the solid and the vaporous compounds.

Conclusions

Being aimed at a new type of porous solids (Fig. 1), a moduled design strategy of new tectonic compound structures has been developed, making use of the conjugation between a shape defined artificial backbone and the particular binding behaviour of bioinspired molecular fragments to act as a specific type of functional end cap. The shape persistency of the synthetic core unit is considered by using particular rigid and geometrically defined linear and tetrahedral aromatic, ethynylene and aliphatic building blocks and spacers, while the molecular fragments derived from biological molecules refer to nucleobases and their derivatives (Fig. 2). Following this approach, the hybrid compounds **1–13** (Fig. 3–5 and Table 1), differing in the overall molecular geometry and the connected nucleobase or nucleobase derivative such as uracil, adenine, adenosine, guanosine and acetyl or isobutanoyl substituted analogs, have been synthesized. The nucleosides including the acetyl as well as the isobutanoyl derivatives were used since they are easier to handle in solution compared to the pure nucleobases.

Except the linear prototype compound **1**, which was obtained *via* Eglinton coupling from 5-ethynyluracil (Fig. 7), all the other compounds **2–13** involve a Sonogashira–Hagihara coupling process between the corresponding ethynyl containing spacer elements and halogenated nucleobase derivatives as the key reaction step (cf. Fig. 8). Selected conditions with reference to the catalytic system, *i.e.* catalyst, solvent, temperature and reaction time, have been tested in view of optimal conversion. In one case, compound **4**, the pure adenine end groups were liberated by acid hydrolysis of the corresponding adenosine. Moreover, the asymmetrically substituted compound **8**, featuring different nucleobases at both ends of the rigid rod, requires a stepwise assembly with the use of a blocking group. All these compounds were obtained as powdery solids that show high melting points (>300 °C) or decompose before melting, except the acylated guanosines which posses lower melting points.

The compounds are rather difficult to dissolve in common organic solvents and resist crystallization to single crystals suitable for an X-ray structural study, except the parent compound **1** which crystallized from DMSO in an adequate manner. The corresponding crystals turned out to be a solvate with DMSO featuring the solvent molecules incorporated in a hydrogen bonded layer structure.

Fluorescence measurements performed of the different compounds in solution show dependencies of the emission maxima and intensities on the nature of the central spacer unit and the capping nucleobase derivative, giving rise to a new structural type of luminescent molecules with fluorescent property controllable by the used building blocks. However, at present, the addition of a complementary nucleobase or a nucleobase derivative, as a possible analyte, to the solutions of the selected compounds

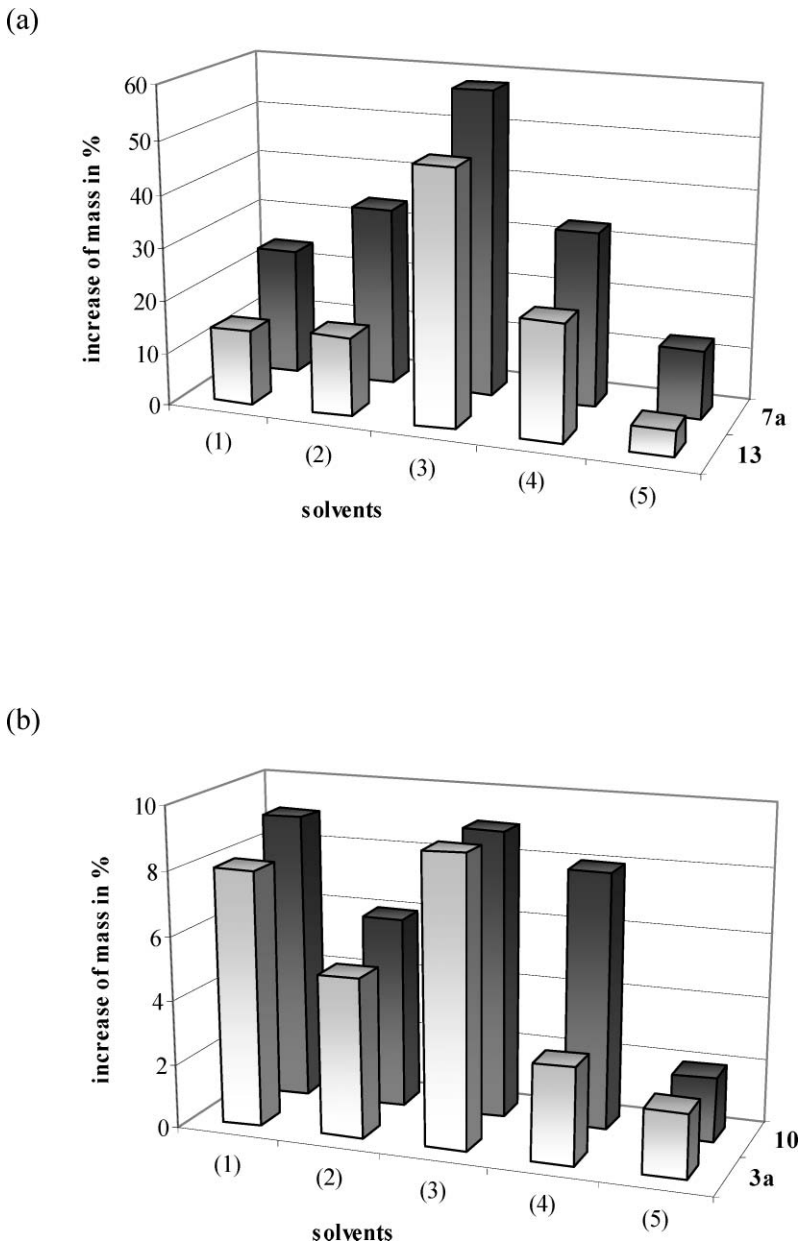


Fig. 13 Comparison of the responses of a QMB device coated with (a) guanosine derivatives **7a** and **13a**, and (b) adenosine derivatives **3a** and **10** for vapours of various solvents: (1) ethanol, (2) acetone, (3) dichloromethane, (4) tetrahydrofuran, (5) *n*-hexane.

resulted in no change of the fluorescence spectra suitable for a practical use in chemical sensing.

Experiments to test the sorption property of a selection of solids of the present compounds with reference to a variety of organic vapours, investigated by quartz micro balance, demonstrated an obvious selectivity in the sorptive behaviour with dichloromethane adsorbing the best and *n*-hexane the worst. This behaviour was most pronounced in the case of the studied guanosine derivatives **7a** and **13**, while the linear and tetrahedral adenosine derivatives **3a** and **10** provide a rather strong developed sorption of ethanol but show a distinct difference in the sorption of THF. All this behaviour is likely to be connected with both the stability of the solid packing structure and the polarity interrelation between the adsorbed compound and the solid adsorbent.

Although the new compounds proved difficult to crystallize in three dimensional bulk habitus, they are more promising for a potential bottom-up layer type immobilization on surfaces.[49] In particular, the linear molecules are expected to act as corresponding self-assembly building blocks due to the sticky nucleobase end groups.[50] In this context, ordered assemblies of this type should result in appealing nanostructured aggregates because of their potential applications in the realm of nanotechnology.[51] It is also possible that molecules of this and related structures are used as designed connecting pieces giving rise to electric conductivity between biological systems.[52] Another interesting aspect relates to a potential topochemical solid state reactivity of the uracil spacer molecules initiated by light to yield cyclobutane dimerization products,[53] possibly as a new type of polymeric material.

Experimental section

General

The nucleobases, nucleosides and the catalytic species were purchased from ABCR (uracil, $[Pd(PPh_3)_2]Cl_2$) and ACROS ORGANICS (adenosine, guanosine, $Pd(OAc)_2$, $[Pd(PPh)_4]$), and were used without further purification. THF was freshly distilled over sodium/benzophenone. Solvents for Sonogashira–Hagihara coupling reactions were deoxygenated prior to use by ultrasound (20 min) while bubbling argon through the solution. All reactions were carried out under an argon atmosphere. TLC was performed on aluminium plates coated with SiO_2-60F_{254} (MERCK). For column chromatography MERCK silica gel 60 (0.040–0.063 mm) was used. Evaporation refers to removal of solvent under reduced pressure using a rotary evaporator. Melting points were obtained on a hot stage microscope PHMK (Rapido, Dresden) and are uncorrected. IR spectra were recorded as KBr pellets on a Nicolet 510 FT-IR spectrometer. NMR spectra were obtained using a Bruker DPX-400 spectrometer at 400.1 MHz (^{1}H) or 100.6 MHz (^{13}C) and a Bruker DPX-500 spectrometer at 500.1 MHz (^{1}H) or 125.8 MHz (^{13}C); measurements were carried out at 25 °C with TMS as an internal standard. Coupling constants are given in Hz and resonance multiplicities are described as s (singlet); br s (broad singlet); d (doublet); br d (broad doublet); dd (double doublet); t (triplet); m (multiplet). The assignment of ribose protons is recorded according to IUPAC nomenclature of sugar moieties. Because of low solubility, solution ^{13}C-NMR spectra could not be obtained for compounds **8** and **9**. Mass spectra were recorded using the following instruments: Hewlett Packard 5890 Series II/MS 5971 A (**9**, **16**, **17**), Varian/Ion Spec QFT FT-ICR (**2a–2c**, **3a**, **3b**, **5a**, **7a**), Finnigan MAT 8200 (**3c**, **4**, **8**), Bruker Daltonics Ultraflex-II TOF-TOF (**9**, **10**, **12**), Bruker Daltonics MALDI-MS Biflex III (**5b**, **5c**, **6a-6c**, **7b**, 7**c**, **13**), Bruker Daltonics Esquire-LC (**18**) and Agilent Technologies (USA) 6890N/5973N MSD (**19**). The fluorescence measurements were accomplished on a Spex FluoroMax-3 spectrofluorometer.

The following compounds were prepared according to literature protocols: 1,4-diethynylbenzene,[34] and 4,4′-diethynyltolane[54] (from MEBYNOL and the corresponding aryl bromides followed by deprotection), 4-ethynyl-1-(trimethylsilylethynyl)benzene[55] (from 1,4-diethynylbenzene with *n*-BuLi and trimethylchlorosilane), 5-iodouracil[28] (from uracil and iodine monochloride), 8-bromoadenosine,[29] 8-bromoguanosine,[30] 8-bromo-2′,3′,5′-tri-*O*-acetylguanosine[31] (by acetylation of guanosine followed by bromination), 8-bromo-2-*i*-butyramido-9-(2′3′5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-6-one[32] (by reaction of 8-bromoguanosine with *i*-butanoyl chloride) and 5-ethynyluracil[28] (from 5-iodouracil and trimethylsilylacetylene followed by deprotection).

5,5′-(1,3-Butadiyne-1,4-diyl)diuracil (1). 5-Ethynyluracil (0.50 g, 4.0 mmol) was added to a suspension of copper(II) acetate (0.38 g, 2.0 mmol) in pyridine/methanol (1:1, 10 cm^3). The mixture was heated to reflux for 4 h, then allowed to cool down to room temperature and poured into sulfuric acid (9 N). The precipitate was filtered off and washed with hot water and diethyl ether. Recrystallization from DMF afforded a light cream coloured powder (0.26 g, 26%); mp > 300 °C (dec.) (lit.[56] mp > 240 °C).

General procedure (Pd(0) catalyzed coupling reaction) for the synthesis of compounds 2, 3, and 5–14

The respective halogenated nucleobase or nucleoside derivative and the corresponding terminal ethynyl compound were dissolved in a degassed mixture of triethylamine (TEA) and *N*,*N*-dimethylformamide (DMF) or toluene. To this solution, the catalyst, being composed of tetrakis(triphenylphosphane)-palladium(0) (TTPd) or bis(triphenylphosphane)palladium(II) chloride (BTPdCl) and copper(I) iodide (CuI), was added and the mixture was stirred at room temperature under argon for 5 h. The precipitate was filtered off and washed with hot water, ethyl acetate and diethyl ether, in this sequence, unless otherwise stated. Basic specifications are given below; for details see ESI A–C.†

5,5′-[Benzene-1,4-diyl-di(ethyne-2,1-diyl)]diuracil (2a). 5-Iodouracil, 1,4-diethynylbenzene, TTPd and DMF were used; yellow powder (77%); mp > 300 °C (dec.) from DMF.

5,5′-[Biphenyl-4,4′-diyl-di(ethyne-2,1-diyl)]diuracil (2b). 5-Iodouracil, compound **17**, TTPd and and DMF were used; yellow powder (62%); mp > 300 °C (dec.) from DMF.

5,5′-[Ethyne-1,2-diyl-bis(benzene-4,1-diyl-ethyne-2,1-diyl)]diuracil (2c). 5-Iodouracil, 4,4′-diethynyltolane, TTPd and DMF were used; yellow powder (91%); mp > 300 °C (dec.) from DMF.

8,8′-[Benzene-1,4-diyl-di(ethyne-2,1-diyl)]diadenosine (3a). 8-Bromoadenosine, 1,4-diethynylbenzene, BTPdCl and DMF were used. In modification of the general procedure, the reaction mixture was stirred at 110 °C for 7 h and allowed to cool down to room temperature Toluene was added and the precipitate washed as described. The crude product was redissolved in hot DMF, precipitated with toluene, collected and washed as before to yield a brown powder (73%); mp > 300 °C (dec.).

8,8′-[Biphenyl-4,4′-diyl-di(ethyne-2,1-diyl)]diadenosine (3b). 8-Bromoadenosine, compound **17**, BTPdCl and DMF were used; brown powder (64%); mp > 300 °C (dec.).

8,8′-[Ethyne-1,2-diyl-bis(benzene-4,1-diyl-ethyne-2,1-diyl)]diadenosine (3c). 8-Bromoadenosine, 4,4′-diethynyltolane, BTPdCl and DMF were used; brown powder (89%); mp > 300 °C (dec.).

8,8′-[Benzene-1,4-diyl-di(ethyne-2,1-diyl)]diguanosine (5a). 8-Bromoguanosine, 1,4-diethynylbenzene, TTPd and DMF were used. In variation of the general procedure, the reaction mixture was stirred for 16 h at 70 °C and allowed to cool down to room temperature. Dichloromethane was added, the precipitate filtered off, stirred in boiling water, separated, washed with water, stirred in ethyl acetate, separated and washed with ethyl acetate, dichloromethane and in this sequence diethyl ether to yield an orange-yellow powder (97%); mp > 300 °C.

8,8′-[Biphenyl-4,4′-diyl-di(ethyne-2,1-diyl)]diguanosine (5b). 8-Bromoguanosine, compound **17**, TTPd and DMF were used; orange-yellow powder (92%); mp > 300 °C.

8,8′-[Ethyne-1,2-diyl-bis(benzene-4,1-diyl-ethyne-2,1-diyl)]-diguanosine (5c). 8-Bromo-guanosine, 4,4′-diethynyltolane, TTPd and DMF were used; orange-brown powder (97%); mp > 300 °C.

8,8′-[Benzene-1,4-diyl-di(ethyne-2,1-diyl)]bis(2′,3′,5′-tri-*O*-acetylguanosine) (6a). 8-Bromo-2′,3′,5′-tri-*O*-acetylguanosine, 1,4-diethynylbenzene, TTPd and DMF were used. In variation of the general procedure, the mixture was stirred for 8 h at 50 °C. The solvent was evaporated and the residue stirred in boiling water. The collected solid was washed with water, stirred in ethyl acetate, separated and washed with ethyl acetate and diethyl ether to afford an orange powder (85%); mp 270 °C (dec.).

8,8′-[Biphenyl-4,4′-diyl-di(ethyne-2,1-diyl)]bis(2′,3′,5′-tri-*O*-acetylguanosine) (6b). 8-Bromo-2′,3′,5′-tri-*O*-acetylguanosine, compound **17**, TTPd and DMF were used; orange powder (72%); mp 220 °C (dec.).

8,8′-[Ethyne-1,2-diyl-bis(benzene-4,1-diyl-ethyne-2,1-diyl)]bis-(2′,3′,5′-tri-*O*-acetylguanosine) (6c). 8-Bromo-2′,3′,5′-tri-*O*-acetylguanosine, 4,4′-diethynyltolane, TTPd and DMF were used; orange powder (87%); mp 240 °C (dec.).

1,4-Bis{[2-*i*-butyramido-6-oxo-9-(2′,3′,5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-8-yl]ethynyl}benzene (7a). 8-Bromo-2-*i*-butyramido-9-(2′3′5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-6-one, 1,4-diethynylbenzene, TTPd and toluene were used. In modification of the general procedure, the mixture was stirred for 5 h at 50 °C. The solvent was evaporated and the residue stirred in boiling water, then collected, washed with water and dried. Purification by column chromatography (SiO_2, eluent: diethyl ether, then CH_2CH_2/MeOH, 9:1) yielded an orange-brown powder (90%); mp 215 °C (dec.).

4,4′-Bis{[2-*i*-butyramido-6-oxo-9-(2′,3′,5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-8-yl]ethynyl}biphenyl (7b). 8-Bromo-2-*i*-butyramido-9-(2′3′5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-6-one and compound **17**, TTPd and toluene were used. Column chromatography with diethyl ether/MeOH (gradient 98:2–25:75) as eluent yielded a yellow-orange powder (63%); mp 145–150 °C.

4,4′-Bis{[2-*i*-butyramido-6-oxo-9-(2′,3′,5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-8-yl]ethynyl}tolane (7c). 8-Bromo-2-*i*-butyramido-9-(2′3′5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-6-one, and 4,4′-diethynyltolane, TTPd and toluene were used. Column chromatography with *n*-hexane/ethyl acetate (1:2) yielded a yellow powder (51%); mp 145–148 °C.

1-[(6-Amino-9-β-D-ribofuranosyl-purine-8-yl)ethynyl]-4-[(2,4-dioxo-1H,3H-pyrimidine-5-yl)ethynyl]benzene (8). 8-Bromo-adenosine, compound **15**, TTPd and DMF were used. In modification of the general procedure, the reaction mixture was stirred at 50 °C for 11 h to yield a brown powder (27%); mp > 300 °C (dec.).

8,8′,8″,8‴-[Methanetetrayl-tetrakis(benzene-4,1-diyl-ethyne-2,1-diyl)]tetrauracil (9). 5-Iodouracil, compound **19**, TTPd and DMF were used; yellow powder (79%); mp > 300 °C (dec.).

8,8′,8″,8‴-[Methanetetrayl-tetrakis(benzene-4,1-diyl-ethyne-2,1-diyl)]tetraadenosine (10). 8-Bromoadenosine, compound **19**, BTPdCl and DMF were used. In modification of the general procedure, the mixture was stirred at 110 °C for 19 h to yield a brown powder (83%); mp > 300 °C (dec.).

8,8′,8″,8‴-[Methanetetrayl-tetrakis(benzene-4,1-diyl-ethyne-2,1-diyl)]tetraguanosine (11). 8-Bromoguanosine, compound **19**, TTPd and DMF were used; orange powder (95%); mp > 300 °C.

8,8′,8″,8‴-[Methanetetrayl-tetrakis(benzene-4,1-diyl-ethyne-2,1-diyl)]tetrakis(2′,3′,5′-tri-*O*-acetylguanosine) (12). 8-Bromo-2′,3′,5′-tri-*O*-acetylguanosine, compound **19**, TTPd and DMF were used; orange-brown powder (97%); mp 266 °C (dec.).

Tetrakis{4-[(2-*i*-butyramido-6-oxo-9-(2′,3′,5′-tri-O-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-8-yl)ethynyl]phenyl}methane (13). 8-Bromo-2-*i*-butyramido-9-(2′3′5′-tri-*O*-*i*-butyryl-*β*-D-ribofuranosyl)-1*H*-purine-6-one, compound **19**, TTPd and DMF were used. In modification of the general procedure, the mixture was stirred for 20 h at 50 °C. The solvent was removed and the residue extracted with chloroform. Evaporation of the solvent yielded a light green powder (96%); mp 106–111 °C.

4-(2,4-Dioxo-1H,3H-pyrimidine-5-yl)-1-[(trimethylsilyl)ethynyl]benzene (14). 5-Iodouracil, 4-ethynyl-1-(trimethylsilylethynyl)benzene, TTPd and DMF were used. In modification of the general procedure, the reaction time was extended to 21 h. From the collected precipitate which had formed, the symmetrical coupling product of the used ethynyl starting compound was isolated (0.36 g; mp 228–232 °C). Partial evaporation of the mother liquor and use of the purification steps described for **2a** yielded **14** as a yellow powder (50%); mp 292–300 °C (dec.).

8,8′-[Benzene-1,4-diyl-di(ethyne-2,1-diyl)]diadenine (4). A suspension of **3a** (0.40 g, 0.61 mmol) in hydrochloric acid (1M, 24 ml) was heated to 100 °C for 4.5 h. The mixture was neutralized with aqueous sodium hydrogencarbonate and cooled for several hours to approx. 0 °C. The precipitate which formed was collected and dried to yield a light brown solid (0.20 g, 83%); mp > 300 °C (dec.).

4-(2-Hydroxy-4-oxo-pyrimidine-5-yl)-1-ethynylbenzene (15). To a solution prepared from finely powdered KOH (11.46 g, 204.0 mmol) in MeOH/THF (1:1, 50 cm^3), compound **14** (0.60 g, 1.95 mmol) was added. The suspension was stirred for 7 h at room temperature. After partial evaporation of the solvent, the precipitate was collected and washed with small portions of MeOH and diethyl ether to yield a yellow powder (0.21 g, 47%); mp > 300 °C (dec.).

4,4′-Bis(3-hydroxy-3-methyl-1-butyne-1-yl)biphenyl (16). To a degassed mixture of 4,4′-dibromobiphenyl (8.30 g, 26.6 mmol), 2-methyl-3-butyn-2-ol (MEBYNOL) (6.30 cm^3, 64.3 mmol), TEA (50 cm^3) and toluene (50 cm^3) were added palladium(II) acetate (80.0 mg, 0.356 mmol), triphenylphosphane (186.7 mg, 0.712 mmol) and CuI (33.3 mg, 0.175 mmol). The resulting mixture was heated to reflux for 8 h. After cooling to room temperature the precipitate was filtered off. The filtrate was evaporated and the residue recrystallized from toluene/2-propanol to obtain a white crystalline powder (5.61 g, 88%); mp 233 °C.

4,4′-Diethynylbiphenyl (17). Compound **16** (5.25 g, 16.5 mmol) was added to a solution prepared from sodium (0.16 g, 7.0 mmol) in 2-propanol (104 cm^3). The resulting mixture was heated to reflux for 3 h. During this time a slight stream of argon was passed through the mixture to remove liberated acetone. After cooling to room temperature, the mixture was diluted with diethyl ether (100 cm^3) and washed with water (5 × 50 cm^3). The organic

layer was dried over Na_2SO_4 and the solvent evaporated. The light yellow residue was recrystallized from 2-propanol to yield a yellow-white crystalline powder (2.18 g, 65%); mp 167–168 °C (lit.[56] mp 167–169 °C).

Tetrakis[4-(3-hydroxy-3-methyl-1-butyne-1-yl)phenyl]methane (18). To a suspension of tetrakis(4-bromophenyl)methane (5.53 g, 8.7 mmol) and 2-methyl-3-butyn-2-ol (MEBYNOL) (13.60 cm^3, 139.2 mmol) in TEA (140 cm^3) were added palladium(II) acetate (156.3 mg, 0.696 mmol), triphenylphosphane (365.1 mg, 1.392 mmol) and CuI (132.6 mg, 0.696 mmol). The resulting mixture was heated to reflux for 11 h. After cooling to room temperature, the precipitate was filtered off and washed with diethyl ether (3×50 cm^3). The combined filtrates were evaporated to yield an oily residue which was recrystallized from toluene/2-propanol to obtain a light yellow powder (4.03 g, 72%); mp > 300 °C (dec.).

Tetrakis(4-ethynylphenyl)methane (19). Compound **18** (4.41 g, 6.8 mmol) was added to a solution prepared from sodium (4.41 g, 191.8 mmol) in 2-propanol (270 cm^3). The mixture was heated to reflux for 6 h. During this time a slight stream of argon was passed through the mixture to remove liberated acetone. After cooling to room temperature, the mixture was diluted with water (200 cm^3) and extracted with diethyl ether (5×50 cm^3). The combined organic extracts were washed with 5% HCl solution (4×50 cm^3) and water (2×50 cm^3). The solvent was evaporated and the resulting residue was purified by column chromatography (SiO_2, eluent: $CHCl_3$) to yield a light yellow powder (2.10 g, 74%); mp > 300 °C (dec.).

Vapour sorption experiments

The experimental setup of the quartz crystal microbalance consists of two 10 MHz standard electronic quartzes with gold electrodes (FOQ Piezo Technik, Germany). One of them is uncoated and used as a reference; the other one is coated with the receptor. Both quartzes are located in a thermostated metal block (controlled to 25 °C by a water thermostat). The measurements are carried out with a constant flow of synthetic air. The resonance frequencies of the quartzes are measured by a multichannel frequency counter (HKR sensor systems Munich, Germany) with a resolution of 1 Hz. The frequency data can be read by the computer *via* a serial interface. The coating of the quarzes was performed by dipping the quartz into a saturated solution of the compound in dichloromethane (**7a**, **13**) or DMF (**2a**, **3a**, **10**). According to the Sauerbrey equation,[57] the measured frequency change is proportional to the increase of mass caused by the adsorbed solvent, which is given as a percentage of the coating. Therefore the adsorption relates to the thickness of the coating and the data meet the requirement for a reasonable comparison.

X-Ray diffraction†

Crystals of **1** suitable for structure analysis were obtained by slow evaporation of a solution of **1** in DMSO. The intensity data were collected on a Bruker APEX II diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å) using ω- and φ-scans. Reflections were corrected for background, Lorentz and polarisation effects. Preliminary structure models were derived by application of direct methods[58] and were refined by full-matrix least squares calculation based on F^2 for all reflections.[59] The hydrogen atoms were included in the models in calculated positions, with the exception of the amino hydrogens H1N to H4N, and were refined as constrained to bonding atoms.

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