Supporting information

Organic/inorganic hybrid filters based on dendritic and cyclodextrin “nanosponges” for the removal of organic pollutants from water

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Table S1. Tested pollutants, their solubility in water (in parenthesis the reference from which it is taken) and chemical affiliation.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Solubility in Water (mg/L)</th>
<th>Group of pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2',4,4',5,5' – Hexachlorobiphenyl</td>
<td>0.0095 (^{(1)})</td>
<td>PCBs</td>
</tr>
<tr>
<td>2,2',4,5,5' - Pentachlorobiphenyl</td>
<td>0.028 (^{(1)})</td>
<td>PCBs</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.073 (^{(2)})</td>
<td>PAHs</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.135 (^{(2)})</td>
<td>PAHs</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.26 (^{(2)})</td>
<td>PAHs</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.29 (^{(2)})</td>
<td>PAHs</td>
</tr>
<tr>
<td>Simazine</td>
<td>6.2 (^{(3)})</td>
<td>Pesticides</td>
</tr>
<tr>
<td>Atrazine</td>
<td>33 (^{(3)})</td>
<td>Pesticides</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>240 (^{(4)})</td>
<td>VOCs</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>1100 (^{(5)})</td>
<td>VOCs</td>
</tr>
<tr>
<td>Benzene</td>
<td>1780 (^{(5)})</td>
<td>BTX</td>
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<tr>
<td>Toluene</td>
<td>515 (^{(5)})</td>
<td>BTX</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>175 (^{(5)})</td>
<td>BTX</td>
</tr>
<tr>
<td>m-Xylene</td>
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<td>BTX</td>
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<tr>
<td>p-Xylene</td>
<td>185 (^{(5)})</td>
<td>BTX</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>2968 (^{(6)})</td>
<td>THMs</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>2510 (^{(6)})</td>
<td>THMs</td>
</tr>
<tr>
<td>MTBE</td>
<td>51600 (^{(7)})</td>
<td>-</td>
</tr>
</tbody>
</table>
General Procedure for the Preparation of acyl substituted cyclodextrin derivatives

For the synthesis of the β-cyclodextrin derivatives CD-8 and CD-18, acylation with the respective n-octyl and octadecyl acyl chlorides at the O2, O3 and O6 positions was accomplished following a method analogous to the one described by Zhang et al. (8). In this case, pyridine was used as a solvent, 4-dimethylaminopyridine as a catalyst and the reaction mixtures were held at 60°C for 3 days. NMR experiments and the fluorescamine test (9) proved that the degree of substitution was more than 98% for the DAB and PEI derivatives and 60-70% for the β-cyclodextrin derivative.

NMR data for the alkyl and acyl substituted compounds

1. Interpreted proton and carbon NMR spectra for alkylated hyperbranched polymers PEI-8, PEI-18

![Chemical structure](image)

\[ R = (-)CH_2-CH_2-H_2n-C_3 \]

\(^1^H\) NMR (250 MHz, CDCl\(_3\)) \(\delta = 6.81\) (s, NCH\(_2\)CH\(_2\)NHCONH), 6.00 (s, (CH\(_2\))\(_n\)CH\(_2\)CH\(_2\)NHCONH), 3.22 (m, NCH\(_2\)CH\(_2\)NHCONH, (NCH\(_2\)CH\(_2\))\(_2\)NCONH), 3.09 (m, (CH\(_2\))\(_n\)CH\(_2\)CH\(_2\)NHCO), 2.80-2.40 (m, NCH\(_2\)CH\(_2\)N, NCH\(_2\)CH\(_2\)NHCONH, (NCH\(_2\)CH\(_2\))\(_2\)NCONH), 1.40 (m, (CH\(_2\))\(_n\)CH\(_2\)CH\(_2\)NHCONH), 1.19 (m, (CH\(_2\))\(_n\)), 0.83 (t, CH\(_3\)).

\(^{12}C\) NMR (62.9 MHz, CDCl\(_3\)) \(\delta = 159.6\) ((NCH\(_2\)CH\(_2\))\(_2\)NCONH), 159.0 (NCH\(_2\)CH\(_2\)NHCONH), 54.0-52.0 (NCH\(_2\)CH\(_2\)N), 49.0-45.0 (NCH\(_2\)CH\(_2\)NHCONH, (NCH\(_2\)CH\(_2\))\(_2\)NCONH), 41.1 ((CH\(_2\))\(_n\)CH\(_2\)CH\(_2\)NHCONH) 40.2 (NCH\(_2\)CH\(_2\)NHCONH), (N(CH\(_2\)CH\(_2\))\(_2\)NCONH), 31.3 (CH\(_2\)CH\(_2\)CH\(_3\)), 30.7 (CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 29.8-29.4 ((CH\(_2\))\(_n\)), 27.2 (NHCONHCH\(_2\)CH\(_2\)CH\(_2\))\(_n\)), 22.7 (CH\(_2\)CH\(_2\)CH\(_3\)), 14.0 (CH\(_3\)).
2. Interpreted proton and carbon NMR spectra for alkylated Dendrimers DAB-8, DAB-18

\[
\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

\(^1\text{H} \text{NMR (250 MHz, CDCl}_3\) \(\delta = 6.40\) (s, NCH\text{2CH}_2\text{NHCONH}), 6.00 (s, (\text{CH}_2\text{n})\text{NCH}_2\text{NHCONH}), 3.25 (m, NCH\text{2CH}_2\text{NHCONHCH}_2\text{CH}(\text{CH}_2)\text{NHCONH}), 2.54 (m, NCH\text{2CH}_2\text{N}, NCH\text{2CH}_2\text{CH}_2\text{N}, NCH\text{2CH}_2\text{N}), 1.55 (m, NCH\text{2CH}_2\text{N}, NCH\text{2CH}_2\text{CH}_2\text{N}, NCH\text{2CH}_2\text{N}), 1.44 (m, NHCONHCH\text{2CH}(\text{CH}_2)\text{NHCONH}), 1.23 (m, NHCONHCH\text{2CH}(\text{CH}_2)\text{CH}_2), 0.85 (t, \text{CH}_3).

\(^{13}\text{C} \text{NMR (62.9 MHz, CDCl}_3\) \(\delta = 159.7\) (CO), 52.5 (NCH\text{2CH}_2\text{CH}_2\text{N}, NCH\text{2CH}_2\text{CH}_2\text{N}), 50.6 (NCH\text{2CH}_2\text{CH}_2\text{NHCONH}), 42.3 (NHCONHCH\text{2CH}_2(\text{CH}_2)\text{NHCONH}), 37.8 (NCH\text{2CH}_2\text{NHCONH}), 31.9 (\text{CH}_2\text{CH}_2\text{N}), 30.6 (\text{CH}_2\text{CH}_2\text{CH}_2\text{N}), 29.8-29.4 (\text{CH}_2\text{CH}_2\text{N}), 27.9 (NCH\text{2CH}_2\text{CH}_2\text{NHCONH}), 27.2 (NHCONHCH\text{2CH}_2(\text{CH}_2)\text{NHCONH}), 24.8 (NCH\text{2CH}_2\text{CH}_2\text{N}, NCH\text{2CH}_2\text{CH}_2\text{CH}_2\text{N}), 22.7 (\text{CH}_2\text{CH}_2\text{CH}_2), 14.1 (\text{CH}_3).


\[
\text{unsubstituted: } R = \text{H} \\
\text{substituted: } R = \text{CO} - \text{C}_7\text{H}_{15} \text{ or } \text{CO} - \text{C}_{17}\text{H}_{35}
\]

\(^1\text{H} \text{NMR (500 MHz, CDCl}_3\) \(\delta = 5.16\) (m, unsubstituted OH-2, OH-3), 4.84 (s, H-1), 4.52 (m, H-3 substitution at O3), 4.49 (s, unsubstituted OH-6), 4.2-3.8 (m, H-6a, H-6b substitution at O6), 3.80-3.53 (m, H-3, H-6a, H-6b no substitution at O3 and O6, H-5, H-2 substitution at O2), 3.50-3.28 (m, H-2 no substitution at O2, H-4), 2.5-2.2 (m, (\text{CH}_2)\text{nCH}_2\text{CH}_2\text{COO}), 1.58 (m, (\text{CH}_2)\text{nCH}_2\text{CH}_2\text{COO}), 1.24 (m, (\text{CH}_2)\text{n}), 0.85 (t, \text{CH}_3).

\(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\) \(\delta = 173.1\) (COO), 102.0 (C-1), 82.6 (C-4), 77.5 (C-3 no substitution) 77.0 (C-2 no substitution) 76.5 (C-5) 73.6 (COOC-3) 73.2 (COOC-2) , 69.6 (COOC-6), 62.3 (C-6 no substitution), 34.0 ((\text{CH}_2)\text{nCH}_2\text{CH}_2\text{COO}), 31.9 (\text{CH}_2\text{CH}_2\text{CH}_3), 30.6 (\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 29.8-29.4 (\text{CH}_2(\text{CH}_2)\text{nCH}_2), 25.0 ((\text{CH}_2)\text{nCH}_2\text{CH}_2\text{COO}), 22.7 (\text{CH}_2\text{CH}_2\text{CH}_3), 14.1 (\text{CH}_3).
Experimental details on the analytical methods

For the determination of THMs, PCBs, MTBE and BTX, a Hewlett Packard GC-5890 Gas-Chromatography instrument was employed, equipped with a split/splitless injector and a multi purpose auto sampler MPS-2 (Gerstel GmbH & Co. KG; BRD). The carrier gas was helium. A fused silica capillary column DB 624 (30 m x 0.53 mm x 3 µm; J&W Scientific, USA) was used for the separation of THMs, BTX or MTBE, with the following temperature program: 50 °C, hold for 1 min, 10 °C/min to 160 °C, hold for 2 min. These volatile substances were measured by the head-space method, introducing 1 mL from the gas phase in equilibrium with the water sample, after conditioning the sample for 20 min at 80 °C. For the determination of PCBs, the water sample was extracted with hexane (200:1), and 10 µL from the hexane extract were injected, separated by an Ultra-1 capillary column (25 m x 0.2 mm I. D., 0.33 µm; Agilent Technologies, USA) and measured with the following temperature program: 120 °C, 40 °C/min to 215 °C, 5 °C/min to 290 °C.

For the determination of the concentrations of pesticides and PAHs a Hewlett Packard HPLC-1090 instrument was employed. A MP-PAH column (250 mm x 3.0 mm I. D., S-5µm; OmniChrom, BRD) was used for the chromatographic separation of pesticides or PAHs. The pesticides (atrazine and simazine) were measured employing a UV-Detector at 220 nm. PAHs were measured by Fluorescence Detector (FLD) (excitation at 260 nm, emission at 405 nm or 450 nm for anthracene or fluoranthene respectively). The eluent solution was a mixture of acetonitrile (ACN) and deionised water, changing from 50 % to 100 % ACN within 16 min. Eluent flow was 0.4 ml/min and injection volume 50 µL. Under these conditions the retention time of the target substances was 4.8 min for simazine, 5.4 min for atrazine, 11.0 min for anthracene and 11.6 min for fluoranthene.
Literature Cited


