Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

A fluorescent probe for ecstasy

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1. Chemicals. All reagents and solvents were used as received without further purification: nonionic surfactant Pluronic F127, Tetraethoxysilane (TEOS, 99.99%), Chlorotrimethylsilane (TMSCl, ≥98%) and 1,2-Bis(triethoxysilyl)ethane (96%) were purchased from Aldrich. Acetic acid (HOAc, ≥99.7%) and reagent grade dichloromethane (DCM) were purchased from Sigma-Aldrich. Sodium chloride (NaCl) was purchased from Fluka. Dialysis was performed vs. water at room temperature under gentle stirring with regenerated cellulose dialysis tubing (Sigma, mol wt. cut off >12 KDa, avg. diameter 33 mm). A Milli-Q Millipore system was used for the purification of water (resistivity ≥18 MΩ).

2. Nanoparticles Synthesis. We synthesized Pluronic® F127-Silica NanoParticles (PluS NPs) by adapting previously reported procedures.[1] In a typical preparation, 200 mg of Pluronic F127 and NaCl (137 mg) were solubilized at 30 °C under magnetic stirring with 3120 µL of HOAc 1 M. TEOS (90 µL, 0.4 mmol) and 1,2-Bis(triethoxysilyl)ethane (223 µL, 0.6 mmol) were then added to the resulting aqueous homogeneous solution, followed by TMSCl (20 µL, 0.16 mmol) after 150 min. The mixture was kept under stirring for 18 h at 30 °C before dialysis treatments. The dialysis purification steps were carried out *versus* Milli-Q water on a precise amount of NPs solution (1500 µL, 24h). The final concentration of the nanoparticle solution was measured taking into account the volume after the dialysis.[1]

3. Dynamic Light Scattering. PluS NPs and **1@PlusNPs** hydrodynamic diameter (d_H) distributions determination was carried out through Dynamic Light Scattering measurements with a Malvern Nano ZS instrument equipped with a 633 nm laser diode. Samples were housed in disposable polystyrene cuvettes of 1 cm optical path length, using water as solvent. The width of DLS hydrodynamic diameter distribution is indicated by Polydispersion Index (PdI). In case of a mono-modal distribution (gaussian) calculated by means of cumulant analysis, $PdI=(\sigma/Zavg)^2$, where σ is the width of the distribution and Zavg is average diameter of the particles population respectively. No change in nanoparticle diameter distribution was observed upon loading of 1. DLS measurements showed no aggregation of the NPs even after several months.

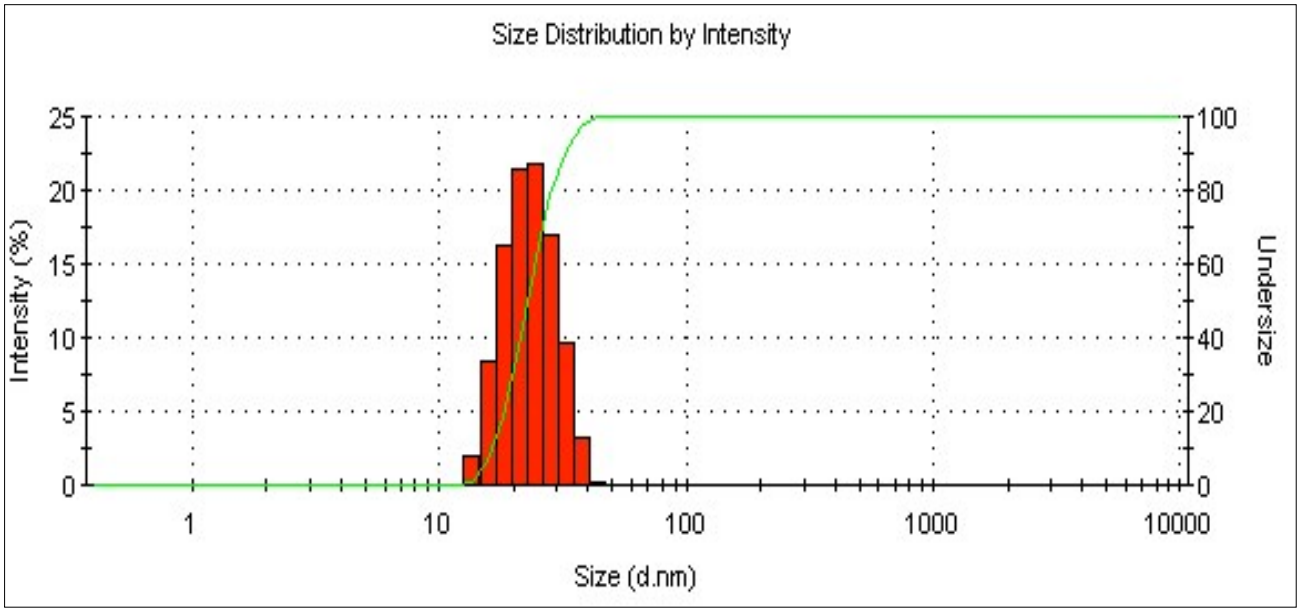


Figure S1. Dynamic light scattering diameter distribution by intensity and undersize curve for **1@PlusNPs** (d_H = 23 nm; PdI = 0.03, water, 25°C).

4. Transmission Electron Microscopy Experiments. A Philips CM 100 TEM operating at 80 kV was used. For TEM investigations, a holey carbon foil supported on conventional copper microgrids was dried up under vacuum after deposition of a drop of NPs solution diluted with water (1:50). We obtained the size distribution by analyzing images with a block of several hundred NPs.

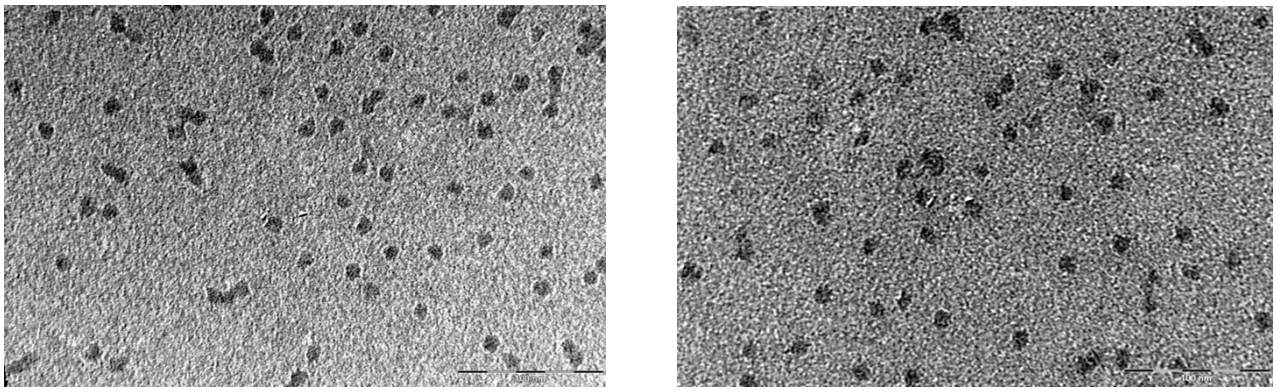


Figure S2. TEM images of PluS NPs (silica core size distribution, d_c = 12 ± 2 nm).

5. Photophysical Measurements. All NP solutions show very weak light scattering and can be treated from the photophysical point of view as any solution of molecular species. UV-Vis absorption spectra were recorded at 25 °C by means of Perkin-Elmer Lambda 45 spectrophotometer. Quartz cuvettes with optical path length of 1 cm were used. The fluorescence spectra were recorded with an Edinburgh FLS920 equipped photomultiplier Hamamatsu R928P. The same instrument connected to a PCS900 PC card was used for the TCSPC experiments. Alternatively, fluorescence spectra were also taken on a Perkin Elmer LS50. Fluorescence spectra were corrected for instrumental response according to standard methods.

6. Preparation of 1@PlusNPs. First, **1** was carefully dissolved in acetonitrile in concentration approximately $3*10^{-5}$M. Then, a small aliquot (500 microliters) was added to 25 ml H_2O containing PluS NPs in concentration approximately $6*10^{-7}$M under stirring, together with a small aliquot of HCl (100 HCl 0.01M) in order to ensure that the drugs will remain protonated. NPs concentration was derived by a method developed in our laboratory.[1] This suspension showed a stable excimeric emission and was used for all titrations, which were performed in 3mL quartz cuvettes with optical path 1cm.

7. RhodNPs were synthesized according to a published procedure.[1] RhodNPs showed their ability to host hydrophobic dyes at a short distance from embedded rhodamine dyes, resulting in efficient energy transfer from rhodamine (embedded in the silica core) to hydrophobic dyes (hosted in the shell). We have exploited this well-known ability of RhodNPs to obtain further indication of the inclusion of cavitand **1** in PluS NPs. The excimeric emission of cavitand **1** has a good spectral overlap with the absorption of rhodamine dyes embedded in NPs, and it can thus perform as a good energy donor towards rhodamine. The excimer emission is found to disappear completely when PluS NPs contain rhodamine dyes as in RhodNPs (black line in Figure S3) compared to undoped PluS NPs (red line in Figure S3). This suggest that chemosensor **1** is indeed few nanometer away from rhodamine dyes, i.e. it is efficiently hosted within PluS NPs.

[1] E. Rampazzo, S. Bonacchi, R. Juris, M. Montalti, D. Genovese, N. Zaccheroni, L. Prodi, D. C. Rambaldi, A. Zattoni and P. Reschiglian, *J. Phys. Chem. B,* 2010, **114**, 14605.

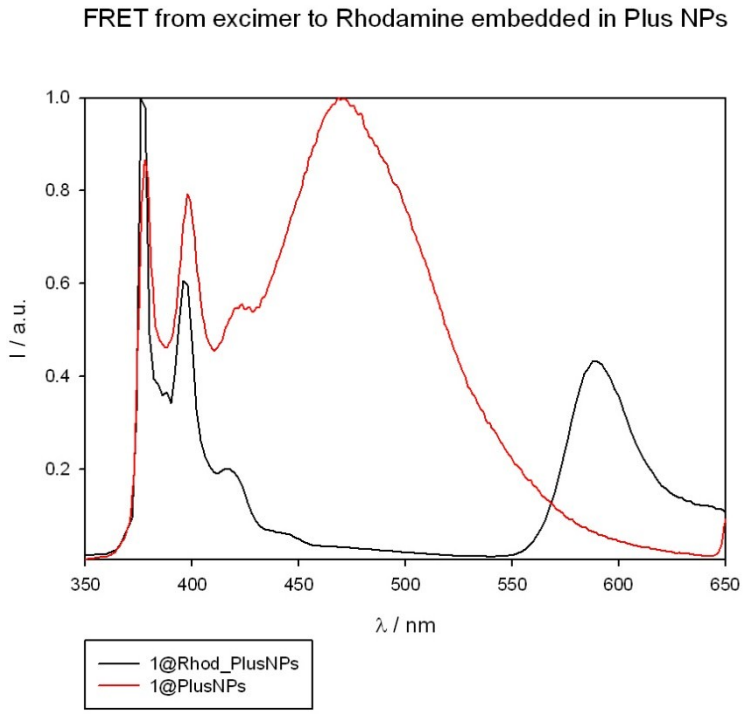


Figure S3. Fluorescence spectra (λ_{exc}=330 nm) of **1@PlusNPs** in H_2O, [**1**]=1x10^{-6} M (red line) and of **1@RhodNPs** in H_2O, in the same conditions (black line). The excimer band is depleted because of FRET is taking place to rhodamine dyes embedded in PluS NPs.

8. Titration Experiments. As prepared solutions of **1@PlusNPs** were titrated with increasing amounts of the interested analyte or interferent (0–0.0025 M in cuvette; mother solutions 0.025M). Absorption and fluorescence spectra (λ_{exc}=330 nm) were acquired after each addition.

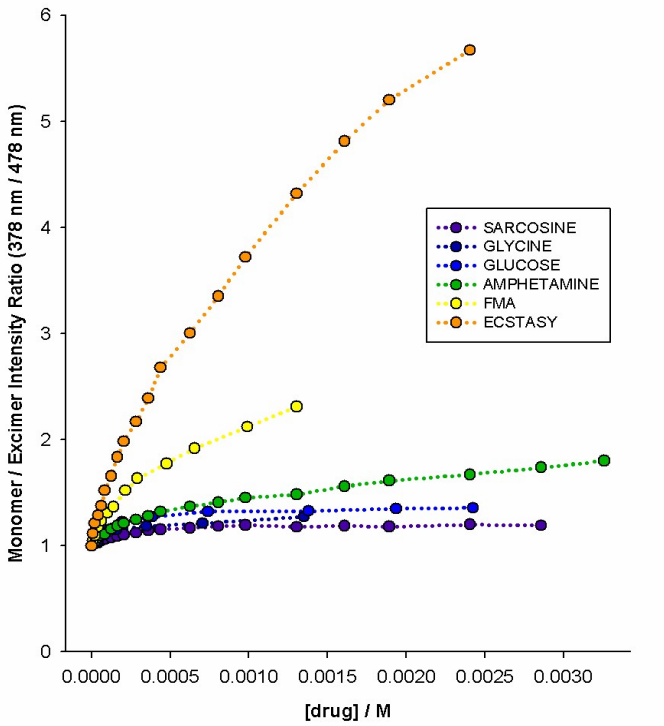


Figure S4. Ratiometric signal Monomer/Excimer, i.e. I(378nm)/I(478nm), for various analytes. Ecstasy (i.e. MDMA) reveals a much enhanced ratiometric signal compared to all other analytes.

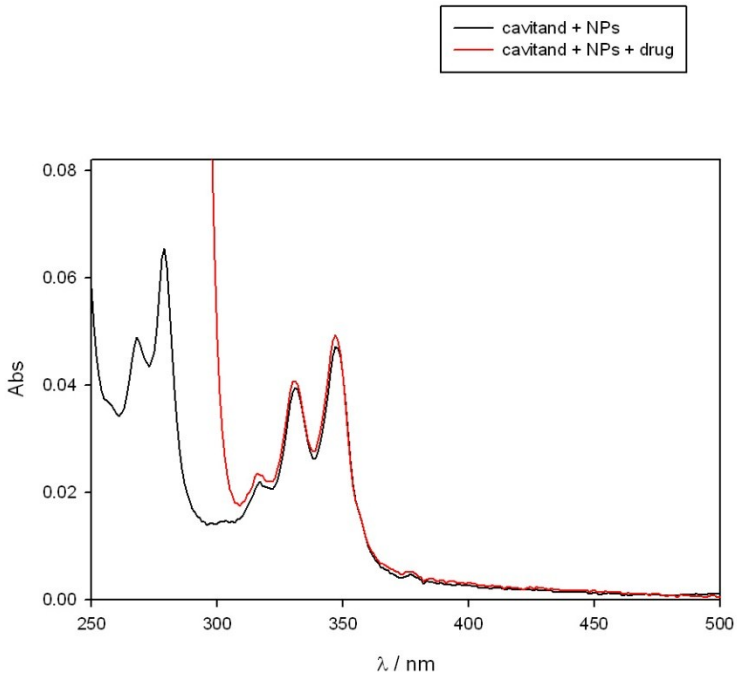


Figure S5. Absorption spectra of **1@PlusNPs** suspension, before (black line) and after addition of 1 equivalent of MDMA (red line). Remarkably, PlusNPs give only a very small scattering contribution, due to their small size and their optimal stability. Furthermore MDMA does not affect absorption spectra in the region of the excitation wavelength (330 nm) and in general on the pyrene absorption bands, as expected for the inhibition of the excimer formation, which occurs at the excited state and not at the ground state.

9. Chemicals and methods. All reagents and chemicals were obtained from commercial sources and used without further purification. Dry pyridine (supplied from Aldrich) was distilled over KOH and stored over 3 Å molecular sieves under Ar or used as received (pyridine absolute, over molecular sieves, $H_2O \leq 0.005\%$). Dichloromethane (purchased from Aldrich) was dried by distillation over CaH_2 according standard procedures and stored over 3 Å molecular sieves under Ar. Anhydrous chloroform (supplied from Aldrich) was prepared washing it twice with water and passed through a column of basic alumina oxide (supplied from Fluka) then it was distilled over CaH_2 and stored over 4 Å molecular sieves under Ar. Anhydrous toluene (supplied from Aldrich) was distilled over CaH_2 and stored over 4 Å molecular sieves under Ar. Dry DMF (DMF purissim. ≥ 99.5%(GC)) was provided by Aldrich and stored over 4 Å molecular sieves under Ar.
Silica column chromatography was performed using silica gel 60 (Fluka 230-400 mesh ASTM), or silica gel 60 (MERCK 70-230 mesh).

- NMR Measurements

^1H NMR spectra were obtained using a Bruker AVANCE 300 (300 MHz) or a Bruker AVANCE 400 (400 MHz) spectrometer. All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. ^{31}P NMR spectra were obtained using a Bruker AVANCE-400 (161.9 MHz) spectrometer. All chemical shifts (δ) were recorded in ppm relative to external 85% H_3PO_4 at 0.00 ppm.

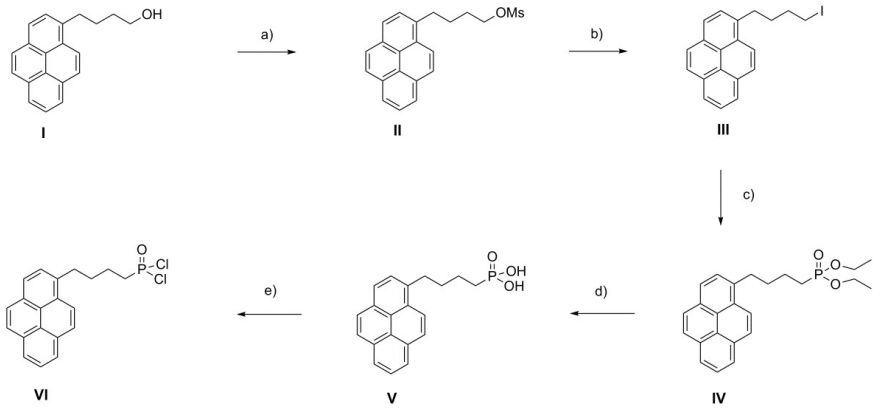
- MS Measurements

Electrospray ionization ESI-MS experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. MALDI was performed on a AB SCIEX MALDI TOF-TOF 4800 Plus (matrix, α–cyano-4-hydroxycinnamic acid).

- MW Reactions

Microwave assisted reaction were performed on a CEM Discover apparatus.

10. Synthesis of chemosensor 2 (compound IX).



Scheme S1. Synthesis of (4-(pyren-1-yl)butyl)phosphonic dichloride, **VI**: a) MsCl, NEt_3, DCM, r.t., 4 h; b) NaI, Acetone, reflux, 4 h, quantitative; c) $P(OEt)_3$, 2 h, microwave power 300 W, 200 °C , 90%; d) HCl 12 N, 2 h, microwave power 300 W, 95%; e) Oxalyl chloride/DMF, $CHCl_3$, 60 °C, 4 h.

4-(pyren-1-yl)butyl methanesulfonate (II): A mixture of **I** (1 g, 3.64 mmol), triethylamine (10.1 mL, 72.8 mmol), mesyl chloride (2.81 m, 36.4 mmol) in dichloromethane was stirred at room temperature for 4 hours. The reaction mixture was quenched with saturated NH_4Cl solution and diluted with ethyl acetate. The organic layer was extracted twice with water, brine and dried over $MgSO_4$. The yellow solid was used without characterizations and further purification in the next step.

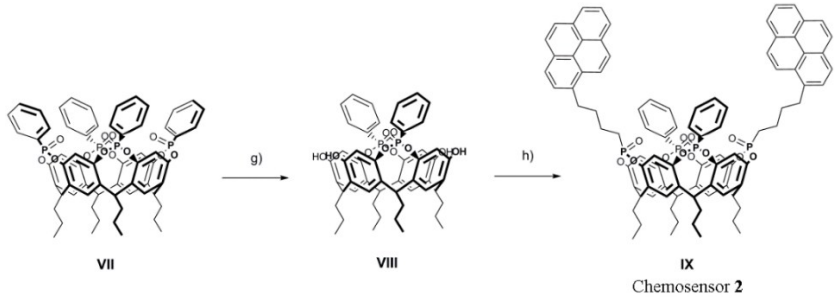
1-(6-iodobutyl)pyrene (III): To a solution of **II** in acetone, NaI (5.4 g, 36.4 mmol) was added. After 4 hours of stirring at reflux the solution was allowed to cool at room temperature and the white solid was filtered off. The resulting solution was dried under reduced pressure and the crude product was purified by silica gel column chromatography (hexane:ethyl acetate 95:5) to give pure **III** as white solid (1.38 g, 3.64 mmol, quantitative yield).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.27 (d, J= 8 Hz, 1H, Ar**H**), 8.20-8.08 (m, 4H, Py**H**), 8.06-7.96 (m, 3H, Py**H**), 7.86 (d, J= 8 Hz, 1H, Py**H**) 3.40-3.34 (m, 2H, PyC**H$_2$**), 3.29-3.22 (m, 2H, C**H$_2$**I), 2.05-1.93 (m, 4H, $PyCH_2C\mathbf{H_2}C\mathbf{H_2}CH_2I$); **ESI-MS**: mass peak was not found.

Diethyl (6-(pyren-1-yl)butyl)phosphonate (IV): III (1.38 g, 3.64 mmol) was suspended in triethyl phosphite (6.2 mL, 36.4 mmol). The reaction was conducted at the microwave reactor using the follow parameters: microwave power 300 W, 200 °C, stirring high, reaction time 2 h. The solution was allowed to cool at room temperature and dried under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate:dichloromethane 1:9) to afford pure **IV** as white solid (1.29 g, 3.27 mmol, 90%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.15 (d, J=9 Hz 1H, Py**H**), 8.11-7.97 (m, 4H, Py**H**), 7.97-7.88 (m, 4H, Py**H**), 7.75 (d, J=3 Hz 1H, Py**H**), 4.17-3.97 (m, 4H, P(O)OC**H$_2$**CH3), 3.26 (t, 2H, J=6 Hz, PyC**H$_2$**CH_2), 1.95-1.68 (m, 6H, $PyCH_2C\mathbf{H_2}C\mathbf{H_2}C\mathbf{H_2}P(O)$), 1.29 (t, J=6 Hz, 6H, P(O)OCH$_2$C**H$_3$**); **^{31}P{^{1}H}NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 28.8 (s, P=O); **ESI-MS**: mass peak was not found.

(6-(pyren-1-yl)butyl)phosphonic acid (V): IV (1.29 g, 3.27 mmol) was suspended in HCl 37% (5 mL). The reaction was conducted at the microwave reactor using the follow parameters: microwave power 300 W, 95 °C, stirring high, reaction time 2 h. The solution was allowed to cool at room temperature and the gray solid was recovered by suction filtration to give pure **V** (1.04 g, 3.1 mmol, 95%).
^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 8.35 (d, J= 8 Hz, 1H, Py**H**), 8.30-7.99 (m, 7H, Py**H**), 7.93 (d, J= 8 Hz, 1H, Py**H**), 3.32 (t, 2H, J=8 Hz, PyC**H$_2$**CH_2), 1.90-1.77 (m, 2H, $CH_2C\mathbf{H_2}P(O)$), 1.70-1.46 (m, 4H,

$PyCH_2C\mathbf{H_2}C\mathbf{H_2}CH_2P(O)$); **$^{31}P\{^1H\}$NMR** (DMSO-$d_6$, 161.9 MHz): δ (ppm) = 26.3 (s, P=O); **ESI-MS**: m/z 361 $[M+Na]^+$.

(6-(pyren-1-yl)butyl)phosphonic dichloride (VI): To a solution of **V** (0.281 g, 0.83 mmol) in dry DCM, oxalyl chloride (0.25 mL, 3 mmol) and two drops of dry DMF were added under nitrogen atmosphere. The green solution was stirred for 4 hours at room temperature then the solvent was removed under *vacuo* and the green solid was used without further purification in the next step.
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.27-7.78 (m, 9H, Py**H**), 3.40 (t, 2H, J=8 Hz, $PyC\mathbf{H_2}CH_2$), 2.72-2.57 (m, 2H, $CH_2C\mathbf{H_2}P(O)$), 2.11-1.91 (m, 4H, $PyCH_2C\mathbf{H_2}C\mathbf{H_2}CH_2P(O)$); **$^{31}P\{^1H\}$NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 50.4 (s, P=O); **ESI-MS**: mass peak was not found.



Scheme S2. Synthesis of chemosensor **2** (**IX**): g) Catechol, K_2CO_3, DMF, 85 °C, 5 h, 75%; h) **VII**, *N*-methylpyrrolidine, toluene/$CHCl_3$, 80 °C, 48 h, 10%.

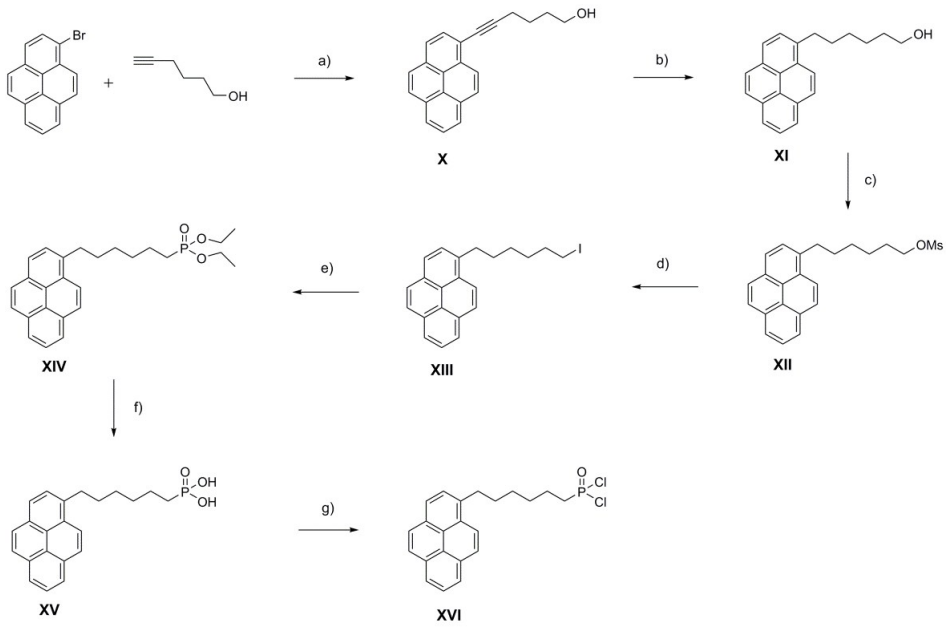
Tiiii[C_3H_7,H,Ph] (**VII**) was synthesized according to literature procedures.[2]

Diphosphonate resorcinarene (VIII): Tetraphosphonate cavitand **VII** (0.86 g, 0.75 mmol) was dissolved in dry DMF then catechol (0.165 g, 1.5 mmol) and K_2CO_3 (1.03 g, 7.5 mmol) were added. The mixture was stirred at 80 °C for 5 hours and quenched by addition of an acidic solution (HCl 10%). The resulting solid was recovered by suction filtration. Purification by silica gel column chromatography (dichloromethane:ethanol 95:5) afforded the pure product **VIII** as white solid (0.5 g, 0.56 mmol, 75%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 9.55 (s, 4H, ArO**H**), 8.14-8.08 (m, 4H, Ar$\mathbf{H_o}$), 7.70-7.68 (m, 2H, Ar$\mathbf{H_p}$), 7.62-7.57 (m, 4H, Ar$\mathbf{H_m}$), 7.11 (s, 4H, Ar**H**), 6.69 (s, 4H, Ar**H**), 4.80 (t, J=8 Hz 2H, ArC**H**), 4.28 (t, J=8 Hz, 2H, ArC**H**), 2.38-2.36 (m, 4H, $C\mathbf{H_2}CH_2CH_3$), 2.05-2.03 (m, 4H, $C\mathbf{H_2}CH_2CH_3$), 1.61-1.55 (m, 4H, $CH_2C\mathbf{H_2}CH_3$), 1.24-1.13 (m, 10H, $CH_2C\mathbf{H_2}C\mathbf{H_3}$), 0.93-0.85 (m, 6H, $CH_2CH_2C\mathbf{H_3}$); **$^{31}P\{^1H\}$NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 6.28 (s, P=O); **ESI-MS**: m/z 902 $[M+H]^+$, 924 $[M+Na]^+$.

Chemosensor 2 (IX): VIII (0.25 g, 0.27 mmol) was dissolved in dry toluene and *N*-methylpirrolidine (0.28 mL, 2.7 mmol). Then **VI** (0.311 g, 0.83 mmol) was dissolved in a mixture 1:1 of anhydrous toluene/chloroform and added dropwise to the resorcinarene solution. The dark green mixture was stirred at 80 °C for 48 hours. The reaction was allowed to cool at room temperature, the residual dark solid was filtered off and the solvent was removed under *vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane:ethanol 95:5) to give the pure product **IX** as yellowish solid (0.04 g, 0.027 mmol, 10%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.28 (d, J=12 Hz, 2H, Py**H**), 8.17-7.94 (m, 18H, Py**H,** P(O)Ar$\mathbf{H_o}$), 7.89 (d, J=8 Hz, 2H, Py**H**), 7.72-7.64 (m, 2H, P(O)Ar$\mathbf{H_p}$), 7.62-7.53 (m, 4H, P(O)Ar$\mathbf{H_m}$), 7.42 (s, 4H, Ar**H**), 6.88 (s, 4H, Ar**H**), 4.80 (t, J=8 Hz, 2H, ArC**H**), 4.59 (t, J=8 Hz, 2H, ArC**H**), 3.49-3.35 (m, 4H, $C\mathbf{H_2}$Py), 2.29-1.96 (m, 20H, $PyCH_2C\mathbf{H_2}C\mathbf{H_2}CH_2P(O)$, $ArCHC\mathbf{H_2}CH_2CH_3$), 1.53-1.31 (m, 8H, $ArCHCH_2C\mathbf{H_2}CH_3$), 1.10 (t, J=8 Hz, 6H, $ArCHCH_2CH_2C\mathbf{H_3}$), 1.03 (t, J=8 Hz, 6H, $ArCHCH_2CH_2C\mathbf{H_3}$); **$^{31}P\{^1H\}$NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 25.1 (s, P=O (butyl-Py)), 10.5 (s, P=O(Ph)); **ESI-MS**: m/z 1528 $[M+Na]^+$; **MALDI TOF-TOF**: calcd. for $C_{92}H_{84}O_{12}P_4$ 1504.4913 Da, found: 1504.3596 Da.

[2] D. Menozzi, E. Biavardi, C. Massera, F.-P. Schmidtchen, A. Cornia, and E. Dalcanale, *Supramol. Chem.,* 2010, **22**, 768.

11. Synthesis of chemosensor 1 (compound XVII).



Scheme S3. Synthesis of (6-(pyren-1-yl)hexyl)phosphonic dichloride, **XVI**: a) $Pd(PPh)_4$, CuI, THF/DIPEA, 50 °C, 12 h, 68%; b) H_2 (2 atm), Pd/C, AcOEt, r.t., 12 h, 94%; c) MsCl, NEt_3, DCM, r.t., 3 h; d) NaI, acetone, reflux, 4 h, quantitative; e) $P(OEt)_3$, 2 h, microwave power 300 W, 200 °C , 85%; f) HCl 12 N, 2 h, microwave power 300 W, 96%; g) Oxalyl chloride/DMF, $CHCl_3$, 60 °C, 4 h.

6-(pyren-1-yl)hex-5-yn-1-ol (X): A mixture of THF/DIPEA (1/1) was degassed 3 times with freeze pump thaw technique followed by addition of 1-bromopyrene (1 g, 3.55 mmol), 5-hexyn-1-ol (0.47 mL, 4.26 mmol), Pd tetrakis(triphenylphosphine) (0.205 g, 0.17 mmol) and CuI (0.067 g, 0.355 mmol). The reaction mixture was stirred for 12 hours at 50 °C and then filtered. Ethyl acetate was added into the solution and extracted twice with saturated NH_4Cl solution and brine, dried with anhydrous $MgSO_4$ and evaporated under reduced pressure to yield a brown oil. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate 6:4) to afford the desired product **X** as yellow oil (0.72 g, 2.41 mmol, 68%).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.56 (d, J=8 Hz, 1H, Py**H**), 8.23-8.00 (m, 8H, Py**H**), 3.81 (t, J=6 Hz, 2H, C**H$_2$**OH), 2.73 (t, J=6 Hz, 2H, C**H$_2$**C≡C), 1.92-1.89 (m, 4H, C**H$_2$**C**H$_2$**OH); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ (ppm) = 135.2, 131.8, 131.2, 131, 130.6, 129.6, 128, 127.7, 127.2, 126.1, 125.5, 125.34, 125.33, 124.4, 124.3, 118.6, 95.9, 80.1, 61.9, 31.7 16.5; **ESI-MS**: m/z 299.4 $[M+H]^+$, 321.4 $[M+Na]^+$, 337.4 $[M+K]^+$.

6-(pyren-1-yl)hexan-1-ol (XI): X (0.72 g, 2.41 mmol) was dissolved in THF and Pd/C (catalytic amount) was added. The mixture was sealed in a Parr reaction bottle and mounted in a shaker hydrogenation apparatus. The air inside the bottle was removed by flushing with hydrogen and a 4 bar of hydrogen pressure was applied. The bottle was shaken for 12 hours at room temperature. The Pd/C was filtered off and the solvent removed in *vacuo* yielded the desired product **XI** as white solid (0.68 g, 2.27 mmol, 94%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.30 (d, J=8 Hz, 1H, Ar**H**), 8.15-7.99 (m, 7H, Py**H**), 7.88 (d, J=8 Hz, 1H, Py**H**), 3.66 (t, J=6 Hz, 2H, C**H$_2$**OH), 3.36 (t, J=6 Hz, 2H, C**H$_2$**Py), 1.90 (m, 4H, C**H$_2$**C**H$_2$**OH); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ (ppm) = 137.1, 131.4, 130.9, 129.7, 128.6, 127.5, 127.2, 127.1, 126.5, 125.7, 125, 124.8, 124.7, 124.6, 123.4, 62.9, 33.5, 32.7, 31.8, 29.5, 25.7; **ESI-MS**: m/z 303.5 $[M+H]^+$, 325.2 $[M+Na]^+$, 341.2 $[M+K]^+$.

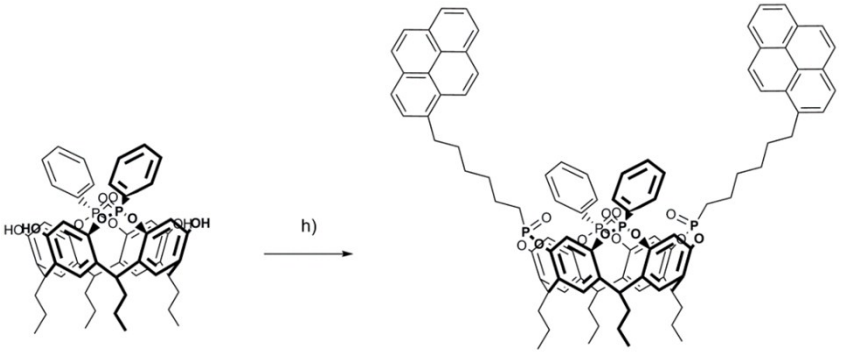
6-(pyren-1-yl)hexyl 4-methylbenzenesulfonate (XII): The synthesis was carried out as compound **II** and used in the next step without characterization and further purification.

1-(6-iodohexyl)pyrene (XIII): The synthesis and purification were carried out as compound **III** (0.93 g, 2.25 mmol, quantitative).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.30 (d, J=12 Hz, 1H, Py**H**), 8.21-8.19 (m, 4H, Py**H**), 8.06-7.97 (m, 3H, Py**H**), 7.89 (d, J=8 Hz, 1H, Py**H**), 3.67 (t, J=8 Hz, 2H, C**H$_2$**Py), 3.37 (t, J=8 Hz, 2H, C**H$_2$**I), 1.96-1.84 (m, 2H, C**H$_2$**CH_2I), 1.67-1.39 (m, 6H, PyCH_2C**H$_2$**C**H$_2$**C**H$_2$**CH_2CH_2I); **ESI-MS**: mass peak was not found.

Diethyl (6-(pyren-1-yl)hexyl)phosphonate (XIV): The synthesis and purification were carried out as compound **IV** (0.8 g, 1.91 mmol, 85%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.26 (d, J=8 Hz, 1H, Py**H**), 8.18-7.93 (m, 7H, Py**H**), 7.85 (d, J=8 Hz, 1H, Py**H**), 4.15-3.99 (m, 4H, C**H$_2$**O), 3.33 (t, J=6 Hz, 2H, CH_2C**H$_2$**Py), 1.92-1.79 (m, 2H, CH_2C**H$_2$**P(O)), 1.79-1.53 (m, 4H, PyCH_2C**H$_2$**CH_2CH_2C**H$_2$**CH_2P(O)), 1.53-1.42 (m, 4H, PyCH_2CH_2C**H$_2$**C**H$_2$**CH_2CH_2P(O)), 1.36-1.24 (m, 6H, C**H$_3$**CH_2O); **^{31}P{^{1}H}NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 27.9 (s, P=O); **ESI-MS**: m/z 423.3 $[M+H]^+$, 445.3 $[M+Na]^+$, 461.2 $[M+K]^+$.

(6-(pyren-1-yl)hexyl)phosphonic acid (XV): The synthesis and purification were carried out as compound **V** (0.67 g, 1.83 mmol, 96%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.35 (d, J=8 Hz 1H, Py**H**), 8.30-8.00 (m, 7H, Py**H**), 7.95 (d, J=8 Hz, 1H, Py**H**), 3.33 (t, J=6 Hz, 2H, CH_2C**H$_2$**Py), 1.83-1.69 (m, 2H, CH_2C**H$_2$**P(O)), 1.60-1.33 (m, 8H, PyCH_2C**H$_2$**C**H$_2$**C**H$_2$**CH_2P(O)); **^{31}P{^{1}H}NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 26.9 (s, P=O); **ESI-MS**: m/z 389.4 $[M+Na]^+$, 405.2 $[M+K]^+$.

(6-(pyren-1-yl)hexyl)phosphonic dichloride (XVI): The synthesis was carried out as compound **VI** and used without further purification.
^{31}P{^{1}H}NMR ($CDCl_3$, 161.9 MHz): δ (ppm) = 51 (s, P=O).



VIII **XVII**
Chemosensor **1**

Scheme S4. Synthesis of chemosensor **1** (**XVII**): h) **VIII**, N-methylpyrrolidine, toluene/$CHCl_3$, 80 °C, 48 h, 12%.

Chemosensor 1 (XVII): The synthesis and purification were carried out as compound **IX** (0.045 g, 0.028 mmol, 12%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.24 (d, J=8 Hz, 2H, Py**H**), 8.16-7.92 (m, 18H, Py**H,** P(O)Ar**H$_o$**), 7.83 (d, J=8 Hz, 2H, Py**H**), 7.72 (bs, 4H, Ar**H**), 7.67-7.59 (m, 2H, P(O)Ar**H$_p$**), 7.55-7.47 (m, 4H, P(O)Ar**H$_m$**), 6.80 (s, 4H, Ar**H**), 4.75 (t, J=8 Hz, 2H, ArC**H**), 4.58 (t, J=8 Hz, 2H, ArC**H**), 3.32 (t, J=8 Hz, 4H, C**H$_2$**Py), 2.58-2.40 (m, 8H, ArCHC**H$_2$**CH_2CH_3), 2.17-2.02 (m, 4H, C**H$_2$**P(O)), 1.92-1.73 (m, 8H, PyCH_2C**H$_2$**CH_2CH_2C**H$_2$**CH_2P(O)), 1.59-1.47 (m, 8H, PyCH_2CH_2C**H$_2$**C**H$_2$**CH_2CH_2P(O)), 1.46-1.32 (m, 8H, ArCHCH_2C**H$_2$**CH_3), 1.13-0.95 (m, 12H ArCHCH_2CH_2C**H$_3$**); **^{31}P{^{1}H}NMR** ($CDCl_3$, 161.9 MHz): δ (ppm) = 25 (s, P=O(hexyl-Py)), 9.9 (s, P=O(Ph)); **ESI-MS**: m/z 803.5 $[M+Na]^{2+}$, 1584 $[M+Na]^+$, 1600 $[M+K]^+$; **MALDI TOF-TOF**: calcd. for $C_{96}H_{92}O_{12}P_4$ 1560.5539 Da, found: 1560.5441 Da.