Electronic Supplementary Material (ESI) for ChemComm.

Probing the in-air growth of large area of 3D functional structures into a 2D supramolecular nanoporous network.

Supporting Information

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Table of content

Materials and methods

Except mentioned in the text, all the solvents and chemical were used as received.

NMR and HRMS spectroscopy

^{1}H and ^{13}C NMR was performed with a Bruker Avance III Spectrometre nanobay 400 MHz (9,4T). HRMS were acquired in the p-ESI mode (MicroTOF, Bruker).

UV Visible spectra

UV Visible spectrum was performed with a Cary Win UV spectrometer, with 1cm path cuves.

Raman spectra

Raman spectra were acquired with an Infinity Spectrometer at two laser wavelengths: 633 nm (P~3 mW) and 532 nm (P ~3 mW). The laser's (width 1µm) was precisely focused on the desired area to analyse, with a x100 zoom. For the HOPG surfaces, measurements were repeated on three different areas of the sample. Powder samples were deposited on a gold mirror prior to measurement.

STM measurements

Scanning Tunneling Microscopy (STM) experiments were performed at room temperature using Keysight STM scanner working with 5100 AFM/SPM microscope system. A drop of solutions containing molecules was applied on a freshly cleaved surface of HOPG (Goodfellow). Pt / Ir STM tips were prepared by mechanical cutting from Pt/ Ir wire (80 / 20, diameter 0.25 mm, Goodfellow). All experiments were repeated several times with different STM tips at different spots on the sample, and the results presented in this work are representative and consistent with the more comprehensive data set. STM images are not corrected for drift. Data analysis and image processing were performed using WSxM software.[1]

Contact angle

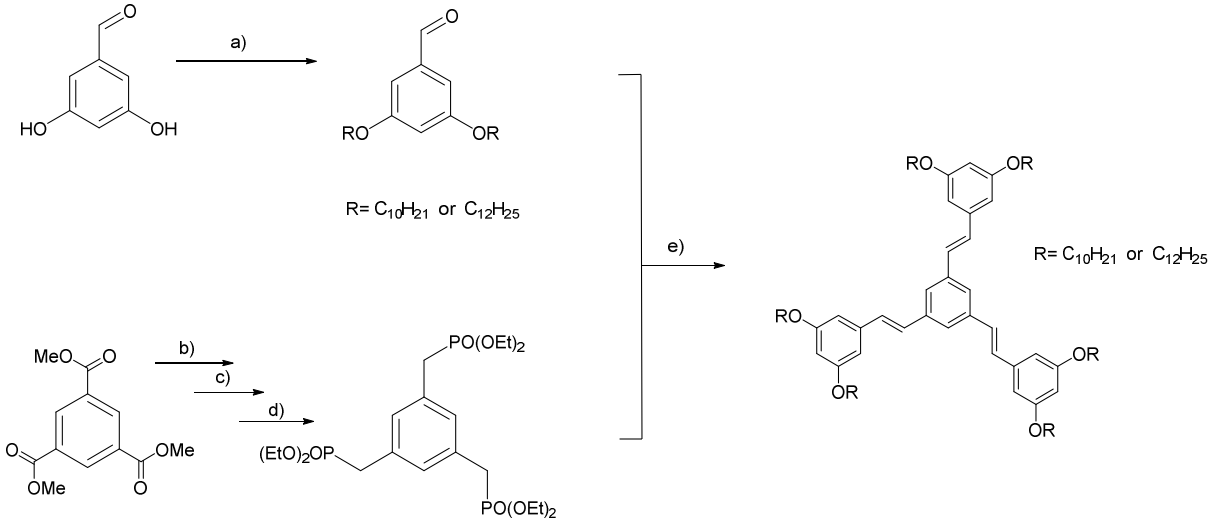
Static water contact angles were measured under ambient conditions (at 20 °C and 40% relative humidity) analyzing the drop profile of sessile drops. A 1 mL droplet of milliQ water was deposited on the sample surface using a Kruss DSA100 apparatus (Germany) equipped with a CCD camera and an image analysis processor. At least three droplets were analyzed on different locations on each sample. A static picture was taken within two seconds after droplet deposition, and angles were measured on the static picture. Three types of measurements were performed on the same angle (two tangent methods and one circle method). The reported values are the averages of these measurements for each kind of HOPG surface. The uncertainty attached to these results follows from the statistical analysis of these repeated experiments. Correction of aberration was done for differences between the means of independent samples being higher than 0.05 (5%).

Organic synthesis

Synthesis of TSB3,5-C_{12}

1,3,5-Tris[(1E)-2-[3,5-bis(dodecyloxy)phenyl]ethenyl]benzene

The synthesis was accomplished according to previous work.[2]

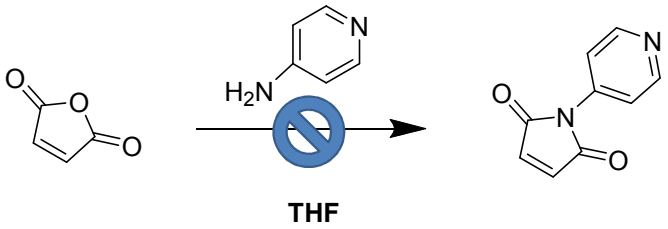


Scheme S1- Synthetic scheme for TSB3,5-C_{12}

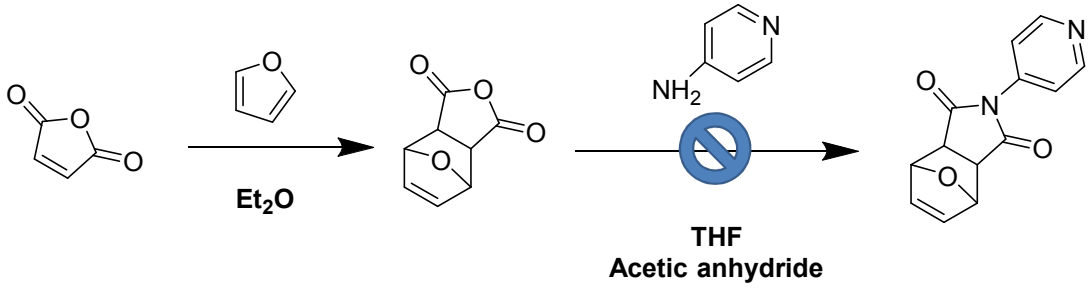
Synthesis of Ligand L

Initial trials

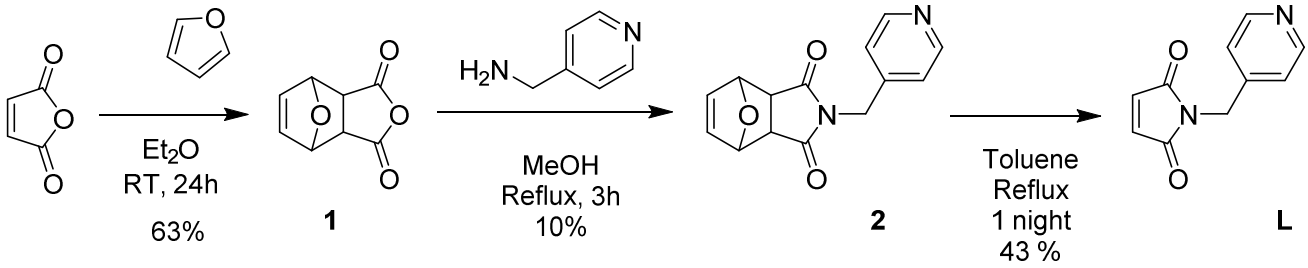
a) First synthetic trial - Direct 4 aminoPyridine conjugation with maleic anhydride



b) Second synthetic trial - Protection of the maleimide double bond via Diels/Alder reaction



Scheme S2- Unsuccessful synthetic trials for the conjugation of 4-AminoPyridine with maleic anhydride.



Scheme S3 - Synthetic route for the Pyridine-Maleimide ligand (L).

Compound 1

The synthesis of **1** was performed according to previous literature.[3]

Compound 2

In a 500 mL one necked flask, **1** (5.0 g, 30 mmol, 1.0 eq.) was mixed with 170 mL of MeOH. 4-Picolylamine (3.3 g, 30 mmol, 1.0 eq.), was dissolved in 35 mL of MeOH and added dropwise to the flask containing **1**, at 0°C (30 min of addition) and under stirring. After 10 minutes at 0 °C, the mixture stirred for one hour at room temperature. The flask was eventually refluxed during 3 hours. The white precipitate formed was discarded by filtration and the filtrate was concentrated to give yellow oil. Compound **2** was crystallized upon the addition of 150 mL hot ethanol and 710 mg (10 % yield) were collected (the crystallization step could be repeated).

NMR (^{1}H, CDl_3, δ in ppm) – 8,534 (**1H**, dd, ^3J=4,4 Hz, ^4J=1,2 Hz); 7,175 (**1H**, dd, ^3J = 4,4 Hz, ^4J=1,6 Hz); 6.533 (**1H**, s); 5,306 (**1H**, s); 4,641 (**1H**, s); 2,912 (**1H**, s).

NMR (^{13}C, J-MOD, δ in ppm) – 174,75 (C_{IV}); 149,20; 143,13 (C_{IV}); 135,66; 121,47; 80,14; 46,66; 40,37 (C_{II})

HRMS (p-ESI, m/z) – $[M-H]^+$: (theoretical: 257,0926; found: 257,0928).

Ligand L

In a 100 mL one necked flask, **2** (300 mg, 1.17 mmol) was mixed with 50 mL of toluene and refluxed during one night. The solvent and the furan adduct were evaporated under reduced pressure and the white solid obtained was recristallized in ethanol to give **L** as a pale yellow solid (100 mg, 43% yield).

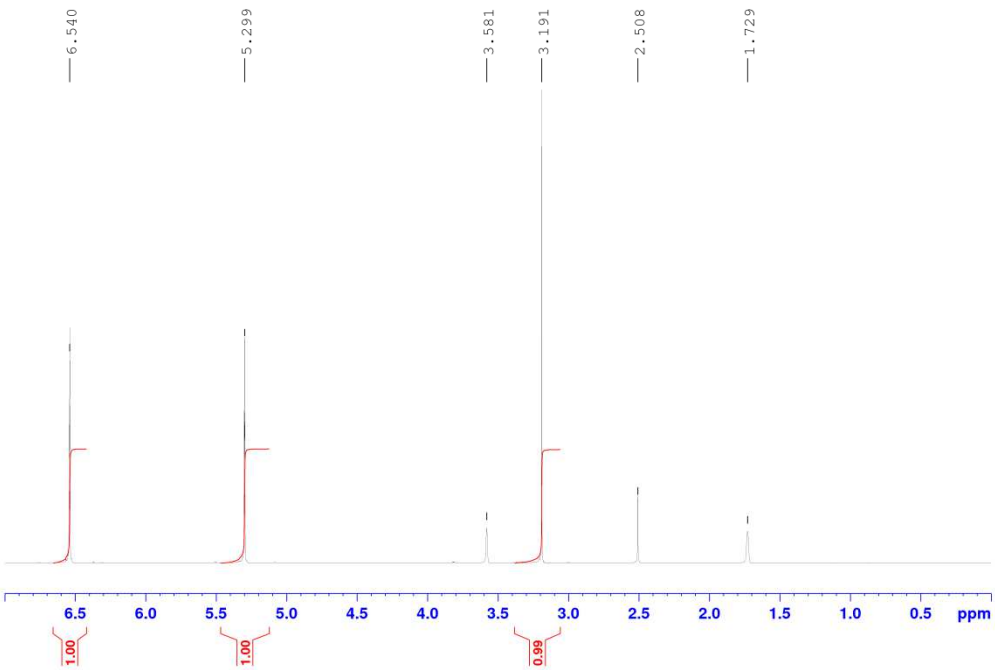
NMR (^{1}H, CDl_3, δ in ppm) – 8,554 (**1H**, dd, ^3J=4,4 Hz, ^4J=1,6 Hz); 7,196 (**1H**, m); 6,762 (**1H**, s); 4,666 (**1H**,s).

NMR (^{13}C, J-MOD, δ in ppm)- 170,16 (C_{IV}); 150,36; 144,79 (C_{IV}); 134,51; 122,90; 40,44 (C_{II}).

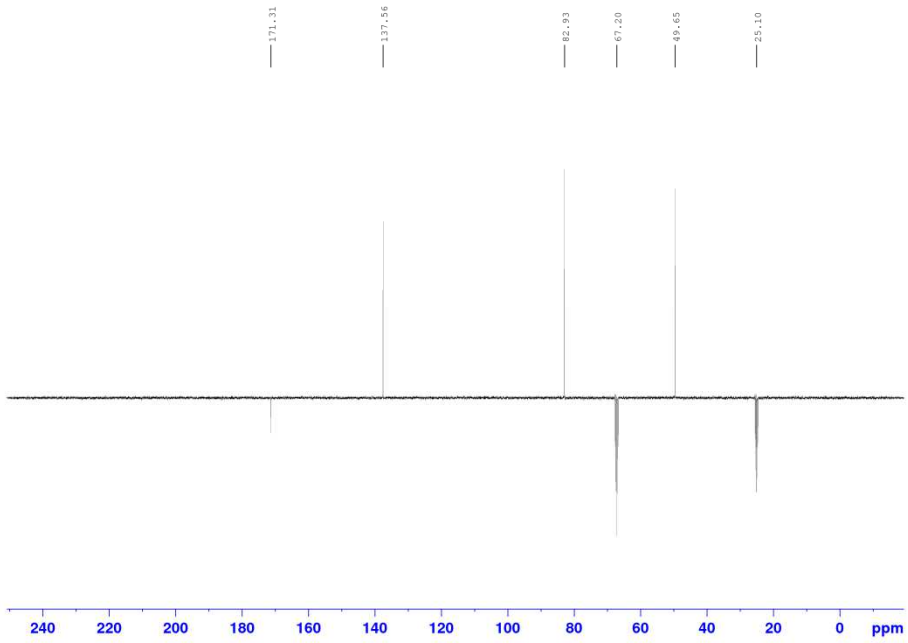
HRMS (p-ESI, m/z) – $[M-H]^+$: (theoretical: 189,064; found: 189,0659).

NMR spectra

Compound 1

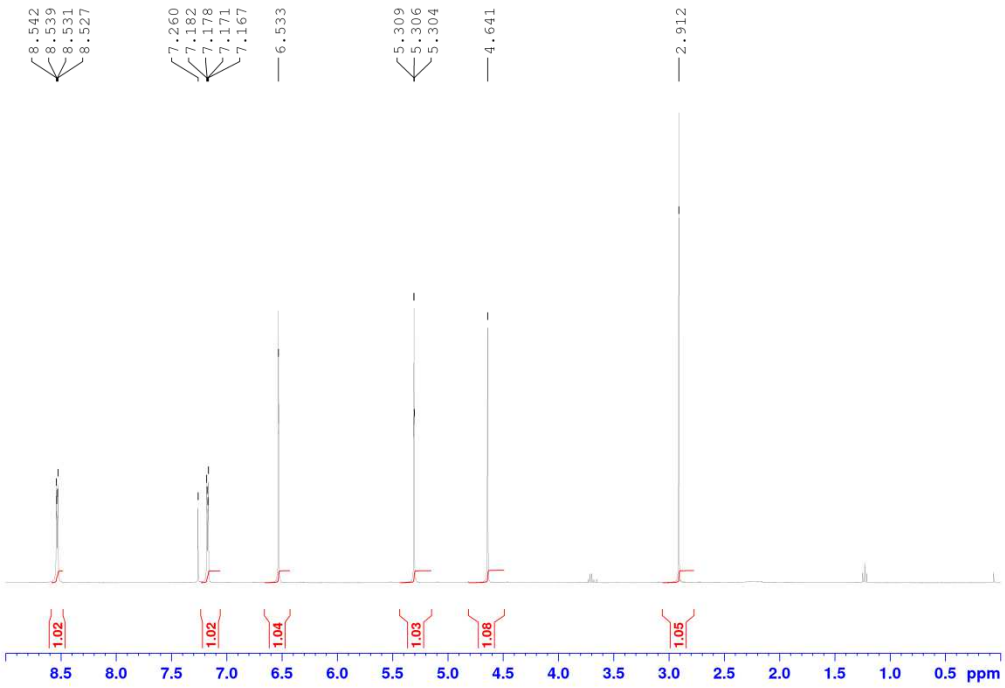


^{1}H NMR spectrum of 1 in THF-d_8

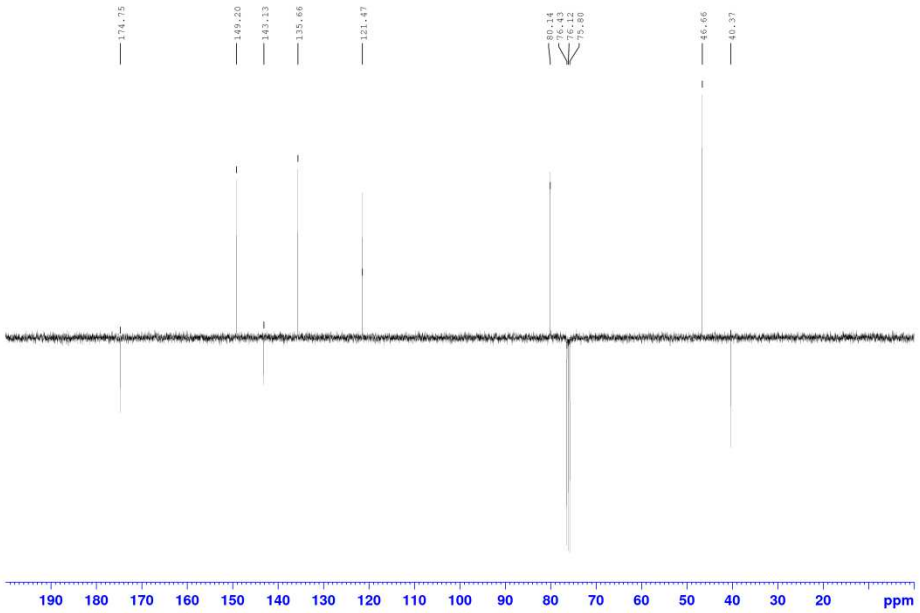


^{13}C NMR spectrum of 1 in THF-d_8

Compound 2

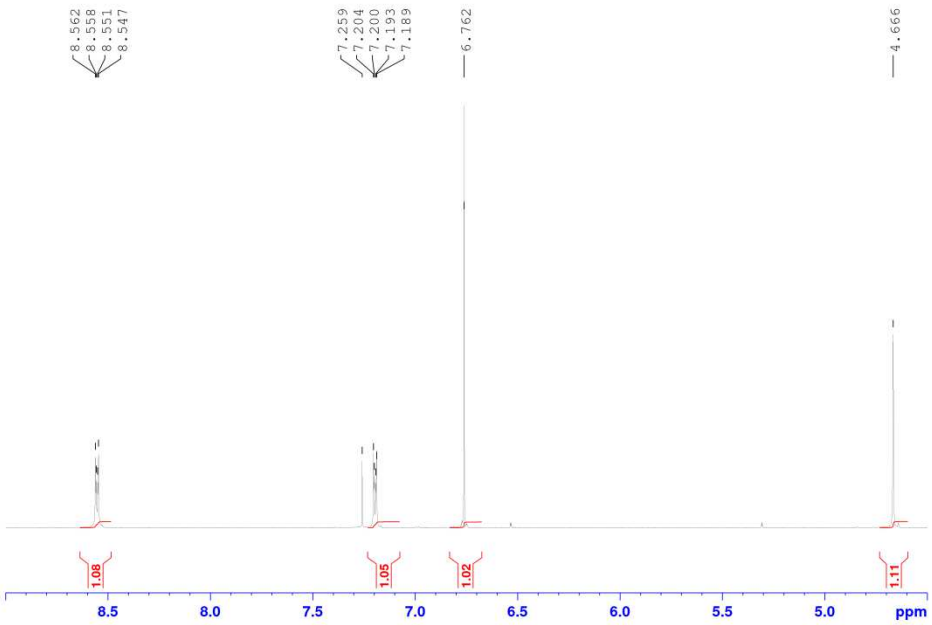


^{1}H NMR spectrum of 2 in $CDCl_3$

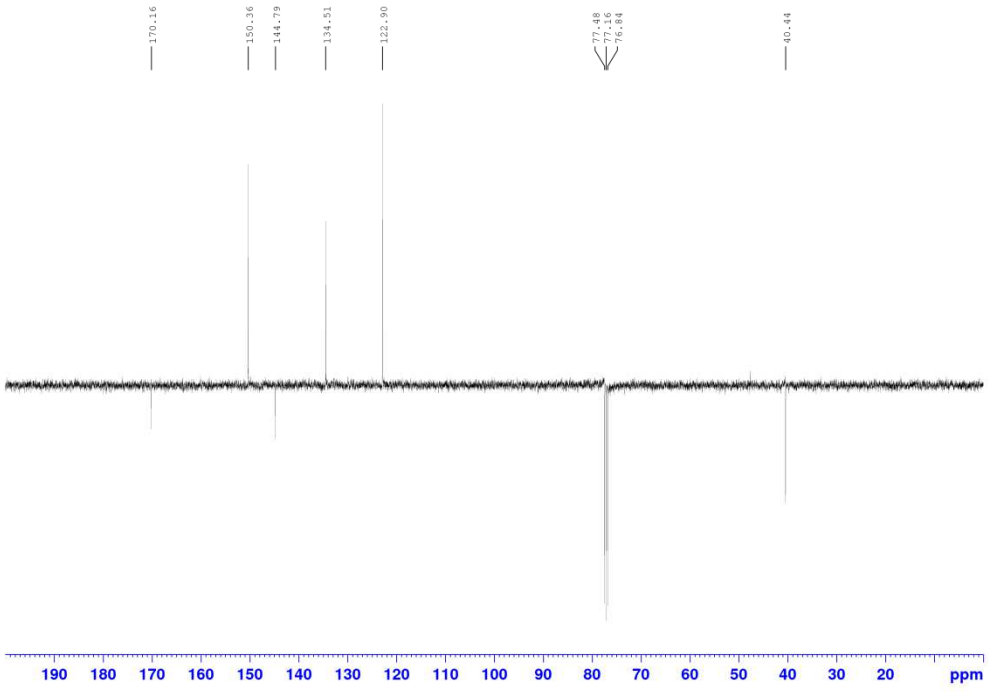


^{13}C NMR spectrum of 2 in $CDCl_3$

Ligand L



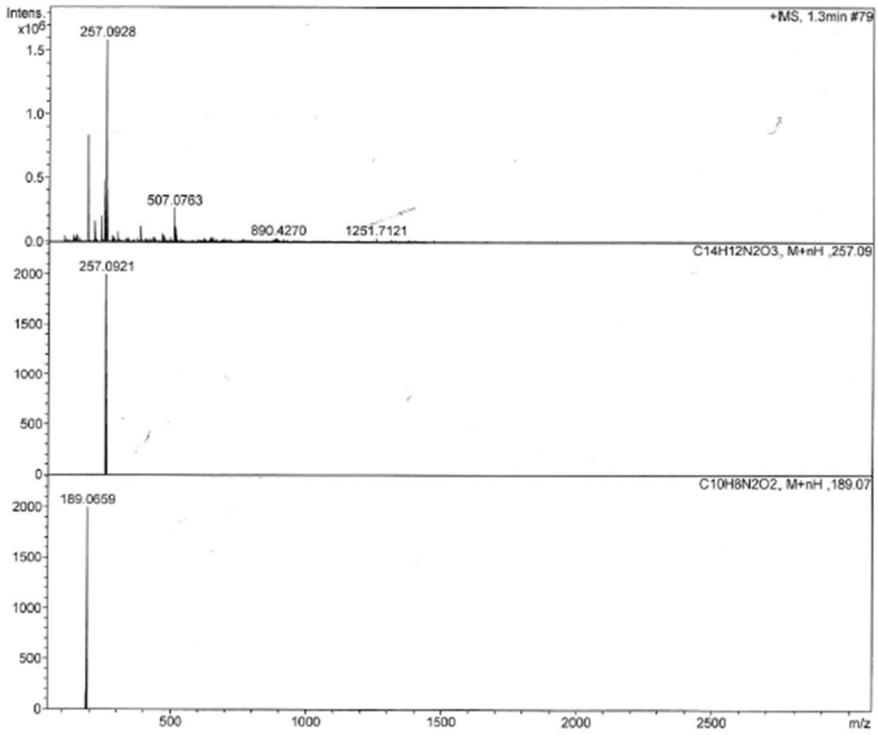
^{1}H NMR spectrum of L in $CDCl_3$



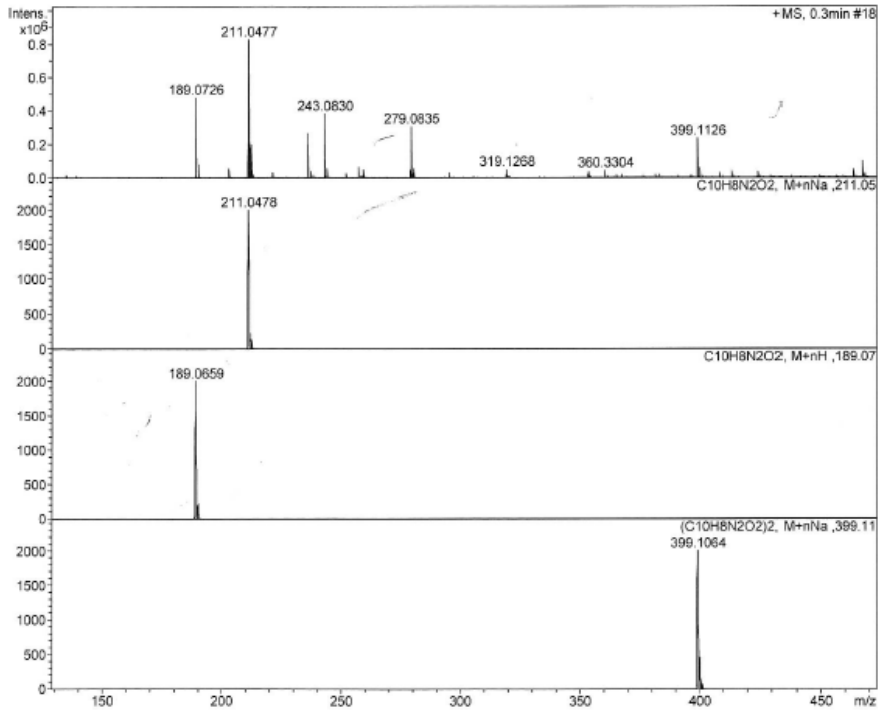
^{13}C NMR spectrum of L in CDl_3

Mass spectra

Compound 2



Ligand L



Preparation of the solutions of ZnPc and of complex ZnPc-L in chloroform

Preparation of the ZnPc solution in chloroform

Because the solubility of **ZnPc** in chloroform is very poor (and would then require large volume of solvents), we first prepared a saturated solution of **ZnPc** from which the excess of compound were removed by centrifugation.The saturated solution of **ZnPc** was prepared by mixing 1.6 mg of sublimated **ZnPc** (480°C/10^{-4} mbar) with 100 mL of chloroform (Carlo Erba, ISO grade). The mixture was stirred in the dark during one hour. Therefore, the appropriate volume of the mixture was centrifuged (4000 RPM/2 min, Ependorf tubes: "Safe Lock tubes – 1.5 mL"), the supernatant was collected. The UV/Visible spectrum of 2,5 mL (3.4 nmol, 1 eq.) of this solution was acquired. The value of the peak absorbance of the Q-band (672 nm) gave the approximate concentration of monomeric ZnPc in the solution at 1.4 µM ($\varepsilon_{ZnPc,672nm,CHCL3}$ = (2.2±1.1)*10^5 see ref[4]).

Titration curve

A concentrated solution of ligand **L** was prepared in $CHCl_3$ (m_{MPy} = 6.7 mg, V_{CHCl3} = 1,1 mL, [**3**] = 33 mM). 1 µL of this solution corresponded to 10 equivalents of **ZnPc**. Gradual aliquots of this solution were taken to make the titration curve, from which the solvent was everytime quickly evaporated. A small portion of the **ZnPc** solution was taken from the cuve and used to solubilise the dried ligand **L**. This mixture was re-introduced in the cuve (no modification of the **ZnPc** solution volume). The spectrum of the obtained solution was acquired.

Preparation of complex ZnPc-L

Complexe **ZnPc-L** was prepared by adding 150 equivalents of ligand **L** to the **ZnPc** solution described above.

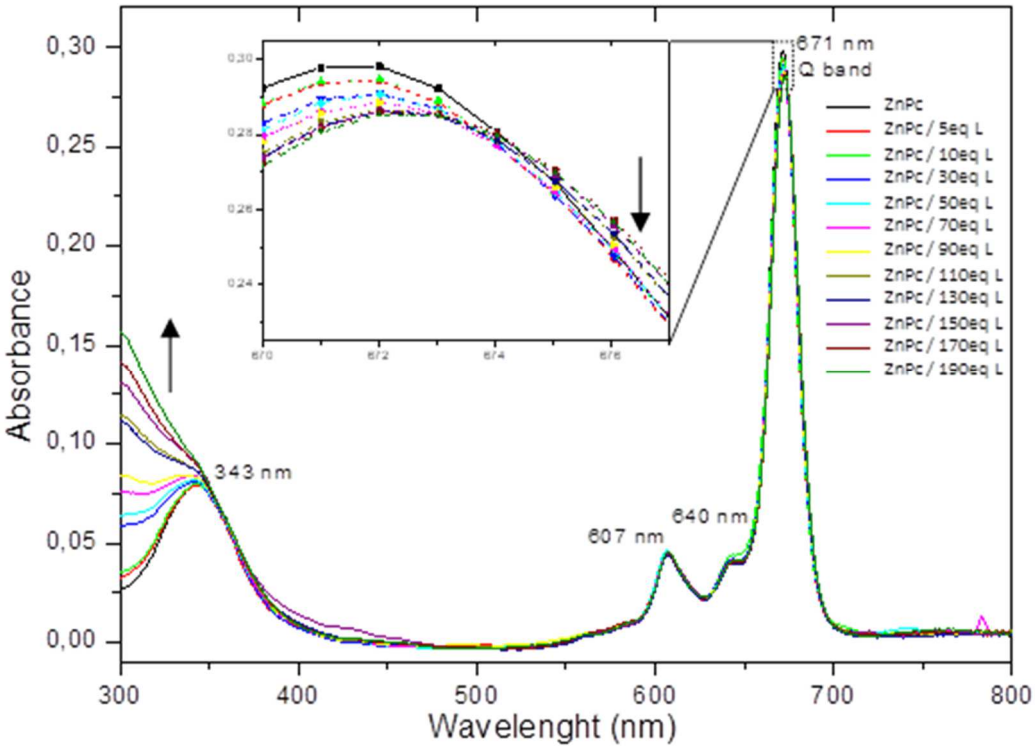


Figure S1: Absorption spectra of ZnPc in presence of different concentrations of ligand L.

Fonctionalisation of the HOPG surface

TSB3,5-C_{12} honeycomb network

A 1.5.10^{-4}M **TSB3,5-C_{12}** solution was prepared in chloroform (m= 3.3 mg in 15 mL) and 20 µL (3 nmol) of this solution were then deposited on freshly cleaved HOPG (1cm^2). All the surface of the freshly-cleaved HOPG was covered. The solvent naturally evaporated quickly and the free **TSB3,5-C_{12}** was removed by generous rinsing of the surface with $CHCl_3$.

Pore filling of the TSB3,5-C_{12} honeycomb network with ZnPc

20 µL (~30 pmol) of the as prepared solution of **ZnPc** complex were deposited on the **TSB3,5-C_{12}** network. The solvent naturally evaporated quickly to give a TSB-OC_{12} network with pores filled with **ZnPc**. The free **ZnPc** was removed by generous rinsing of the surface with $CHCl_3$. This operation was repeated twice.

Pore filling of the TSB3,5-C_{12} honeycomb network with ZnPc-L

20 µL (~30 pmol) of the as prepared solution of **ZnPc-L** complex were deposited on the **TSB3,5-C_{12}** network. The solvent naturally evaporated quickly to give a **TSB3,5-C_{12}** network with pores filled with **ZnPc-L**. The free **ZnPc-L** was removed by generous rinsing of the surface with $CHCl_3$. This operation was repeated twice.

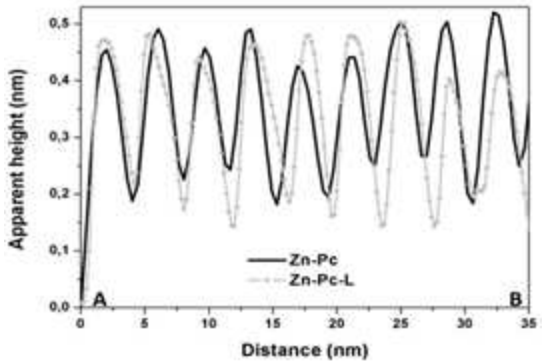


Figure S2. Cross-sections showing apparent height of guest molecules along the black line AB for STM image reported in Fig 2a and 2b, respectively.

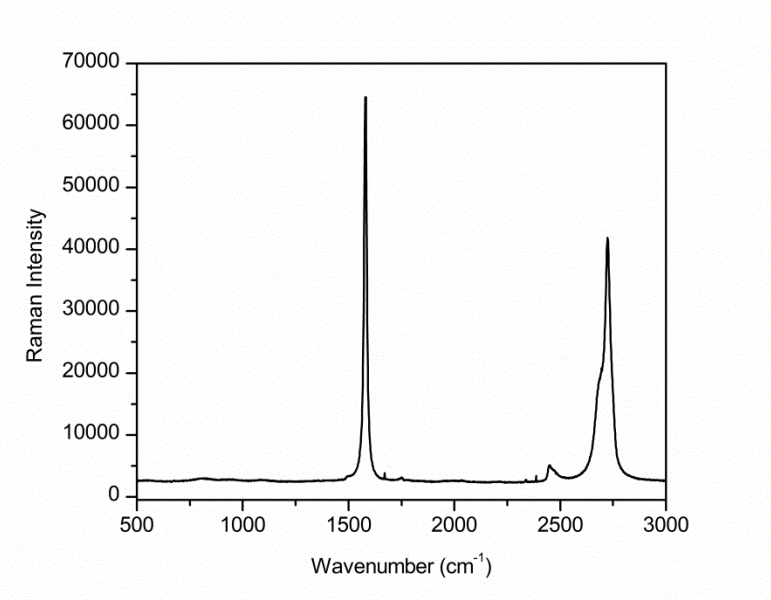
Raman spectra at 633 nm

HOPG//TSB//ZnPc-L Raman Freq. (cm^{-1}) Excitation at 633 nm	Pure ZnPc powder Raman Freq. (cm^{-1}) 633 nm (major bands)
X	591 (w)
680 (w)	680 (m)
748 (w)	749 (m)
827 (w)	829 (m)
948 (w)	948 (m)
X	1010 (w)
1109 (w)	1110 (w)
1142 (m)	1142 (m)
1182 (w)	1183 (w)
1201 (w)	1203 (w)
1219 (m)	1220 (m)
1306 (m)	1306 (m)
1337 (i)	**1339 (i)**
1437 (m)	1440 (m)
1454 (m)	1455 (m)
1517 (i)	**1518 (i)**
1588 (*)	
2467 (*)	
2655 (sh*)	
2695 (*)	

1- Raman Frequencies of HOPG//TSB//ZnPc-L. Excitation wavelength was set at 633 nm. The band with a star (*) are attributed to HOPG. The intensity of the bands are reported between bracket (weak: w; m: medium; i: intense).

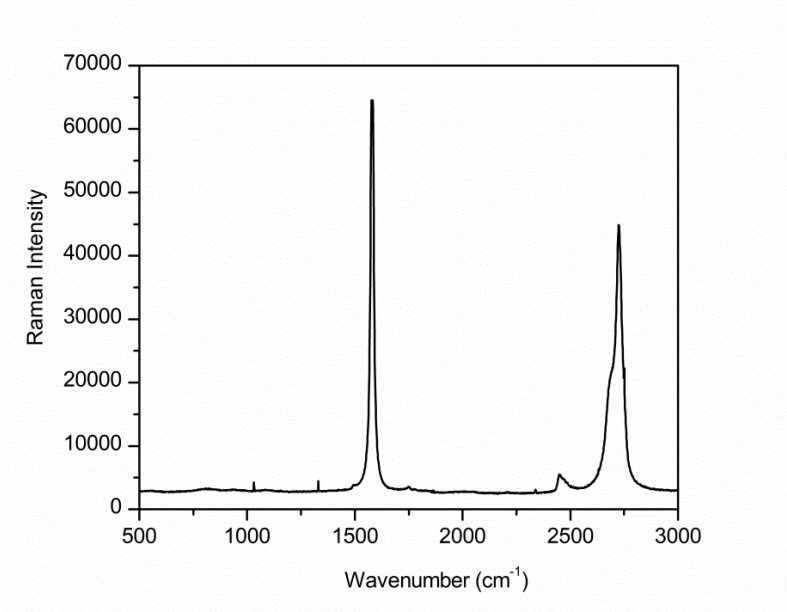
Raman spectra at 532 nm

HOPG//TSB//ZnPc



Raman spectrum of HOPG//TSB//ZnPc electrode – Excitation at 532 nm

HOPG//TSB//ZnPc-L



- Raman spectrum of HOPG//TSB//ZnPc-L electrode – Excitation at 532 nm

ZnPc - Raman Freq. (cm^{-1}), 532 nm	ZnPc-L - Raman Freq. (cm^{-1}) 532 nm
1582	1582
2448	2448
2683 (shoulder)	2683 (shoulder)
2724	2724

Raman Frequencies of a) HOPG//TSB//ZnPc samples b) HOPG//TSB//ZnPc-L. Excitation wavelength was set at 532 nm.

Molecular modeling

Computational methods

The geometries of the pyridine-maleimide ligand **L**, the zinc phthalocyanine complex (**ZnPc**) and the zinc phthalocyanine complex with its additional axial ligand (**ZnPc-L**) were optimized in their electronic ground state and in the gas phase by DFT using the B3LYP hybrid functional [5] and the 6-31G(d) double-zeta basis set. This level of theory was chosen as it has already proven its ability to reproduce with good accuracy the IR and Raman spectra of ZnPc at reasonable computational cost.[6] Vibrational calculations using the harmonic method were then performed at the same level of theory, firstly to ensure that the resulting geometries were true local minima of the potential energy surfaces and secondly to simulate the infrared and Raman spectra of the three molecular entities.

For all these computations, the Gaussian 09 package was used.[7]

Simulations of the Raman spectra were performed using the opensource GaussSum application.[8] This program calculates Raman intensities from Raman activities provided by the Gaussian program using the following formula extracted from the Placzek's polarizability theory [9] :

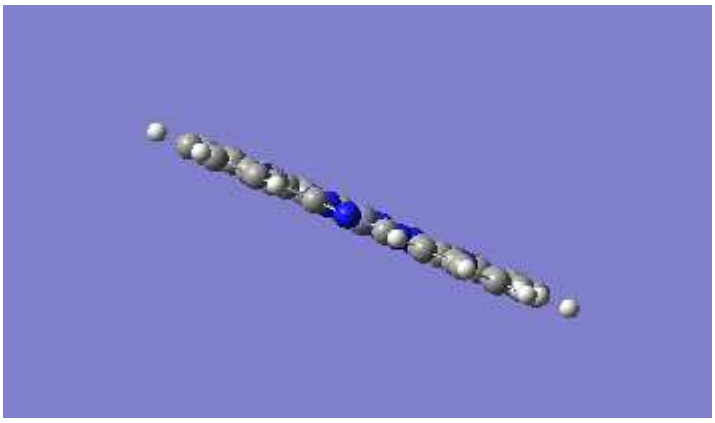
$$I_k = N \frac{(\nu_0 - \nu_k)^4 P}{\nu_k \left(1 - \exp\left(\frac{-hc\nu_k}{k_B T}\right)\right)} S_k$$

where N *N* is a constant, ν_0 the exciting laser wavenumber, ν_k the wavenumber of the k k^{th} normal mode, P *P* the exciting laser irradiance, and S_k S_k and I_k the Raman activity and Raman intensity respectively associated to the k^{th} normal mode.

In order to ease the comparison with experimental spectra, we chose ν_0 = 633 nm (expressed in cm^{-1} unit for its integration in the above formula) for the laser excitation and T = 293 K for the temperature. Note also that the normal mode wavenumbers provided by the Gaussian program were all multiplied by 0.96 (scale factor) as recommended by the Computational Chemistry Comparison and Benchmark Database (CCCBDB) of the National Institute of Standards and Technology (NIST)[10] for the B3LYP/6-31G(d) level of theory.

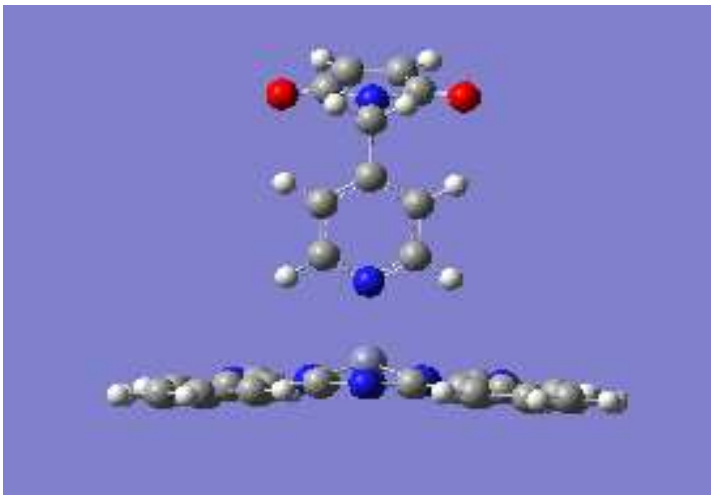
Optimized Geometries

ZnPc



Optimized geometry of ZnPc in vacuum

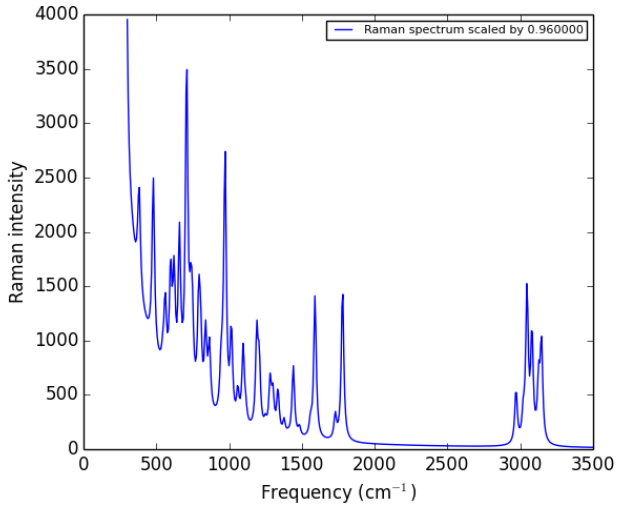
ZnPc-L



Optimized geometru of ZnPc-L in vaccum

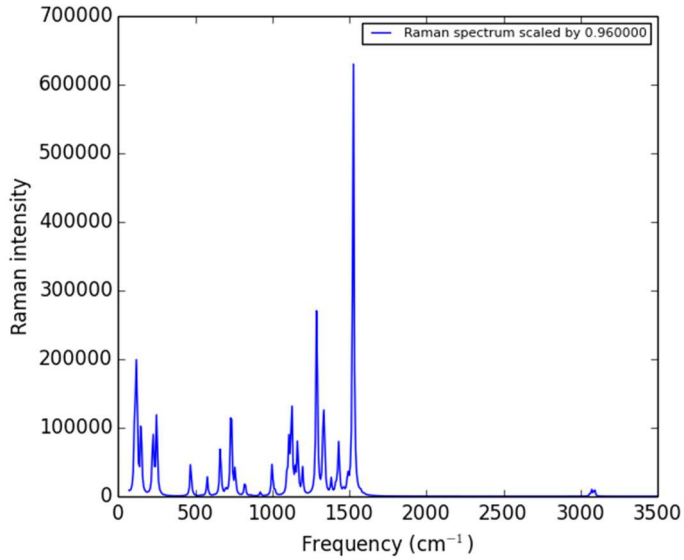
Simulated Raman Spectra

Ligand L



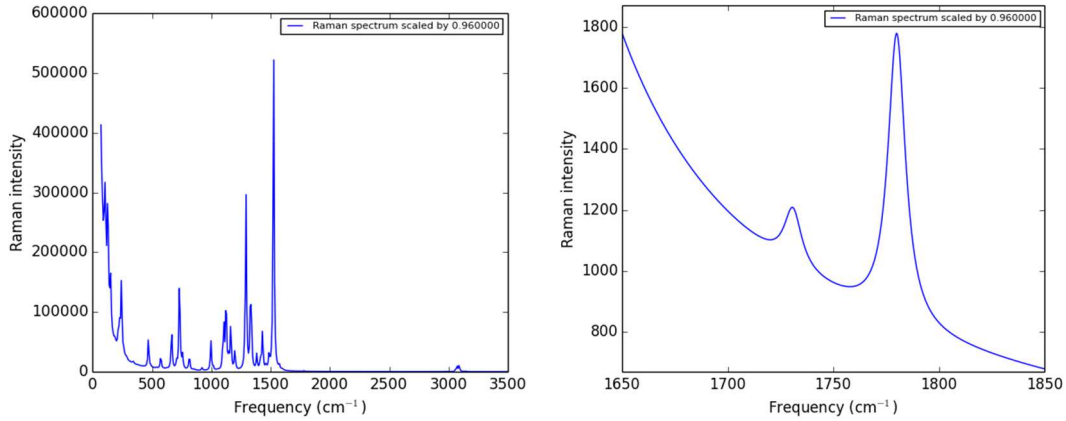
– Simulated Raman spectrum of ligand L in vacuum, with excitation at 633 nm.

ZnPc



- Simulated Raman spectrum of ZnPc in vacuum, with excitation at 633 nm.

ZnPc-L



- Simulated Raman spectrum of ZnPc-L in vaccum. Excitation wavelength at 633 nm. Left: whole spectrum. Right: zoom on the 1750 cm^{-1} region.

Cartesian coordinates for geometries optimized by DFT at the B3LYP/6-31G(d) level of theory, in vacuum

Ligand L

N	-3.63709800	0.00000100	-0.81676300
C	-3.03140900	1.14088500	-0.46358600
C	-3.03141200	-1.14088100	-0.46357400
C	-1.82915800	1.19684500	0.24243300
H	-3.53501700	2.06021000	-0.75846600
C	-1.82916200	-1.19683700	0.24244600
H	-3.53502400	-2.06020800	-0.75844300
C	-1.20790000	0.00000500	0.61083100
H	-1.37988900	2.15354300	0.49371000
H	-1.37989600	-2.15353400	0.49373400
C	0.10818100	0.00000700	1.36558200
H	0.18915600	0.88900700	1.99623300
H	0.18915300	-0.88898700	1.99624200
N	1.27091500	0.00000100	0.48167800
C	1.88526900	1.15063600	-0.02216100
C	1.88526300	-1.15064200	-0.02215200
C	3.00069900	0.66832900	-0.90702300
C	3.00068800	-0.66834700	-0.90702800
H	3.65502000	1.35697600	-1.42599500
H	3.65499800	-1.35700200	-1.42600400
O	1.56241600	2.29363600	0.23000100
O	1.56238700	-2.29363800	0.22999700

ZnPc

N	-0.00012200	1.62173300	1.15414800
C	-0.00013900	1.61839400	2.52723700
N	-0.00011400	0.56176600	3.33489000
C	-0.00006900	-0.70114200	2.91795100
N	-0.00004600	-1.15414300	1.62173600
C	0.00002200	-2.52723500	1.61839400
C	0.00005500	-3.00057200	3.00014000
C	-0.00000100	-1.85155600	3.81783500
C	0.00001900	-1.95761900	5.20905600
C	0.00009200	-3.23708900	5.76285200
C	0.00014800	-4.38422900	4.94650800
C	0.00013300	-4.28024300	3.55621200
H	0.00017800	-5.15971000	2.91987500
H	-0.00002300	-1.06821800	5.83143100
N	0.00008000	-3.33488800	0.56176800
C	0.00008700	-2.91795100	-0.70114200
N	0.00003400	-1.62173700	-1.15414400
C	0.00008500	-1.61839400	-2.52723500
N	0.00007500	-0.56176500	-3.33488500
C	0.00001600	0.70114300	-2.91794900
N	-0.00004400	1.15414800	-1.62173300
C	-0.00007500	2.52723800	-1.61839300
N	-0.00011900	3.33488800	-0.56176400
C	-0.00014000	2.91794900	0.70114400
C	-0.00015200	3.81783300	1.85155800
C	-0.00014900	3.00013900	3.00057400
C	-0.00015200	3.55621200	4.28024500
C	-0.00016300	4.94650800	4.38423000
C	-0.00016700	5.76285100	3.23709000
C	-0.00015900	5.20905400	1.95761900

H	-0.00016000	5.83142900	1.06821900
H	-0.00017500	6.84310000	3.35455100
H	-0.00014800	2.91987500	5.15971200
C	-0.00001000	3.00057400	-3.00013800
C	0.00004400	1.85155700	-3.81783300
C	0.00011600	1.95761900	-5.20905300
C	0.00012800	3.23708900	-5.76285100
C	0.00007500	4.38423000	-4.94650700
C	0.00000800	4.28024500	-3.55621100
H	-0.00003300	5.15971200	-2.91987500
H	0.00015900	1.06821800	-5.83142800
C	0.00018800	-3.00013900	-3.00057100
C	0.00019000	-3.81783400	-1.85155500
C	0.00028300	-5.20905500	-1.95761800
C	0.00037100	-5.76285200	-3.23708900
C	0.00037000	-4.94650800	-4.38422900
C	0.00028000	-3.55621100	-4.28024300
H	0.00028500	-5.83143000	-1.06821800
Zn	-0.00026300	-0.00000200	-0.00000900
H	0.00028000	-2.91987500	-5.15971000
H	-0.00016900	5.41143200	5.36636200
H	0.00008600	5.36636100	-5.41143100
H	0.00018000	3.35455100	-6.84310000
H	0.00044000	-5.41143100	-5.36636100
H	0.00044300	-6.84310100	-3.35455100
H	0.00020600	-5.36636100	5.41143100
H	0.00010700	-3.35455100	6.84310100

ZnPc-L

N	0.23548800	-1.40849100	1.79549700
C	-0.65122800	-1.17545600	2.81326700
N	-1.07824900	0.00009100	3.26861500
C	-0.65118000	1.17560500	2.81322400
N	0.23554500	1.40856500	1.79544400
C	0.45174600	2.75656400	1.68737100
C	-0.36499200	3.45338300	2.68058300
C	-1.06065600	2.45495200	3.39192100
C	-1.92790300	2.78526500	4.43340500
C	-2.08973400	4.13570900	4.74177700
C	-1.39515300	5.13280600	4.03110700
C	-0.52183900	4.80346700	2.99486600
H	0.02244800	5.56576900	2.44584900
H	-2.45476900	2.00961000	4.98067200
N	1.28326400	3.38311700	0.85618700
C	2.10149500	2.75651900	0.01206100
N	2.20597000	1.40846200	-0.20594000
C	3.21038400	1.17544000	-1.10774600
N	3.65936200	-0.00009400	-1.54138900
C	3.21033700	-1.17559500	-1.10770100
N	2.20591300	-1.40854200	-0.20588800
C	2.10138400	-2.75658700	0.01216400
N	1.28312800	-3.38312100	0.85631400
C	0.45163500	-2.75650200	1.68747400
C	-0.36513300	-3.45325100	2.68071200
C	-1.06075700	-2.45476600	3.39201200
C	-1.92801900	-2.78500300	4.43350700
C	-2.08990600	-4.13542900	4.74192900
C	-1.39536500	-5.13258100	4.03129700
C	-0.52203700	-4.80331700	2.99504500

H	0.02222000	-5.56566200	2.44605800
H	-1.54236800	-6.17555900	4.29907800
H	-2.45485400	-2.00930600	4.98074400
C	3.08226100	-3.45335900	-0.81943600
C	3.78289300	-2.45493100	-1.52583000
C	4.81109800	-2.78509000	-2.40879500
C	5.11720500	-4.13552300	-2.57512500
C	4.41737200	-5.13264200	-1.86969400
C	3.39437700	-4.80340200	-0.98082100
H	2.85385100	-5.56574000	-0.42813600
H	5.34995000	-2.00944700	-2.94424500
C	3.78299000	2.45473800	-1.52592400
C	3.08239800	3.45322000	-0.81956800
C	3.39456700	4.80324400	-0.98100500
C	4.41757400	5.13240900	-1.86989200
C	5.11736700	4.13523600	-2.57528600
C	4.81120600	2.78482200	-2.40890300
H	2.85407300	5.56562500	-0.42834900
Zn	0.88490600	-0.00000100	0.46370700
H	5.35002600	2.00913700	-2.94432500
H	-2.76082500	-4.42620000	5.54596800
H	4.68307100	-6.17559900	-2.02057100
H	5.91085900	-4.42625800	-3.25828600
H	5.91103000	4.42591300	-3.25846000
H	4.68331400	6.17535000	-2.02081000
H	-1.54211200	6.17580000	4.29884900
H	-2.76063900	4.42653800	5.54580600
N	-0.65513700	0.00000300	-1.04571300
C	-1.14885400	1.15365500	-1.52593300
C	-1.14887200	-1.15364700	-1.52591900
C	-2.14258500	1.19879200	-2.49790800
H	-0.72620400	2.06436300	-1.11254300
C	-2.14260400	-1.19878100	-2.49789300
H	-0.72623700	-2.06435700	-1.11251800
C	-2.65474500	0.00000700	-3.00379300
H	-2.51952300	2.15463100	-2.84809400
H	-2.51955800	-2.15461700	-2.84806700
C	-3.75579700	0.00000900	-4.04867700
H	-3.68383700	0.88940200	-4.67965000
H	-3.68383500	-0.88938000	-4.67965600
N	-5.08667400	0.00000600	-3.45526400
C	-5.80119100	1.15217500	-3.10693100
C	-5.80118600	-1.15216500	-3.10692900
C	-7.09183500	0.66857500	-2.50906400
C	-7.09183200	-0.66857000	-2.50906300
H	-7.84944400	1.35625300	-2.15592700
H	-7.84943900	-1.35625000	-2.15592500
O	-5.42150300	2.29286000	-3.27369100
O	-5.42149300	-2.29284900	-3.27368600

Calculated vibrational modes (harmonic approximation - B3LYP/6-31G(d))

Ligand L

Unscaled wavenumbers (cm^{-1})	Scaled wavenumbers[a] (cm^{-1})	Infrared intensity ($km.mol^{-1}$)	Raman activity ($Å^4.amu^{-1}$)
26.6755	25.60848	0	5.6463
41.6884	40.020864	0.006	3.6896

53.2844	51.153024	0.5924	5.8735
135.6367	130.211232	12.3472	0.4399
175.7057	168.677472	0.8578	1.6697
204.2205	196.05168	2.9497	1.6157
280.6769	269.449824	7.6331	1.5872
299.5846	287.601216	0.0108	2.1619
349.1777	335.210592	0.5002	0.0128
388.9625	373.404	0.0075	0.1287
397.9747	382.055712	11.6587	1.1115
498.5327	478.591392	17.1078	3.192
566.965	544.2864	0.0584	0.3167
584.0675	560.7048	12.6647	1.8723
623.1998	598.271808	7.8347	3.1597
647.6618	621.755328	15.4583	3.3336
685.788	658.35648	0.1649	5.4663
703.3696	675.234816	32.3115	0.2512
737.3319	707.838624	4.3796	14.1761
765.4417	734.824032	0.3463	2.9033
777.0767	745.993632	6.973	3.6899
824.1136	791.149056	7.4889	5.3153
836.962	803.48352	64.0001	3.6608
873.122	838.19712	10.4314	4.6676
896.5424	860.680704	7.7876	0.804
901.0978	865.053888	8.2438	3.5872
966.6535	927.98736	0.0084	0.0006
983.7811	944.429856	1.9723	3.3994
996.209	956.36064	0.1665	1.5722
1012.4752	971.976192	4.6836	22.5414
1057.2875	1014.996	13.1803	5.7667
1057.6843	1015.37693	0.2691	2.748
1103.4343	1059.29693	2.4909	3.2108
1121.1508	1076.30477	2.9518	0.1748
1142.0351	1096.3537	0.7957	8.8421
1160.7083	1114.27997	34.5888	1.5358
1239.3088	1189.73645	5.8494	12.7505
1256.8507	1206.57667	3.8604	8.8794
1300.9028	1248.86669	3.2177	1.3708
1334.9309	1281.53366	0.0157	8.0387
1354.5157	1300.33507	21.0793	6.0789
1389.8352	1334.24179	169.1384	6.1842
1394.4472	1338.66931	1.9625	1.603
1434.8863	1377.49085	178.1829	2.7149
1463.1493	1404.62333	20.6754	0.3021
1500.5903	1440.56669	31.2291	15.0795
1544.5185	1482.73776	2.6044	2.1455
1623.9771	1559.01802	18.448	3.8112
1655.3876	1589.1721	40.9154	18.3904

1656.7673	1590.49661	2.0147	20.251
1800.7846	1728.75322	494.604	7.9772
1853.031	1778.90976	4.4612	54.8378
3094.5761	2970.79306	12.9142	73.8256
3146.2939	3020.44214	1.2444	34.9018
3171.7825	3044.9112	34.4469	119.0168
3174.2976	3047.3257	17.3535	105.7747
3207.3886	3079.09306	11.3877	7.2159
3208.5808	3080.23757	0.2984	154.5229
3256.5144	3126.25382	0.0995	90.887
3276.6851	3145.6177	0.2763	158.4823

[a] : Scaling factor : 0.96

ZnPc

Unscaled wavenumbers (cm^{-1})	Scaled wavenumbers[a] (cm^{-1})	Infrared intensity ($km.mol^{-1}$)	Raman activity ($Å^4.amu^{-1}$)
16.7409	16.071264	0.4449	0.0003
20.9697	20.130912	0	0
59.0399	56.678304	0.0001	0.3963
59.0399	56.678304	0	0.3963
61.1691	58.722336	0.0001	0
63.2878	60.756288	12.1423	0.0016
112.6369	108.131424	0	12.3444
119.661	114.87456	0.0001	0
119.9461	115.148256	3.1406	0

119.9661	115.167456	3.1331	0
124.3273	119.354208	0	0
125.3966	120.380736	0	11.8889
125.3969	120.381024	0	11.8891
154.6158	148.431168	0	21.508
211.216	202.76736	0.001	0.0001
227.9127	218.796192	0	0
233.8067	224.454432	0.0003	0.0859
233.824	224.47104	0.049	16.2187
234.029	224.66784	0.0576	13.5307
239.0471	229.485216	0.0001	8.2207
239.048	229.48608	0	8.2205
244.7141	234.925536	5.0999	0
244.8171	235.024416	5.0675	0.0261
260.9707	250.531872	0.001	66.3386
287.2239	275.734944	0	0.1481
287.2246	275.735616	0	0.1481
306.4882	294.228672	2.9222	0
306.5167	294.256032	2.9128	0.0004
346.0933	332.249568	2.846	0.0013
435.9901	418.550496	0	0
437.1439	419.658144	0	0.0481
437.1445	419.65872	0	0.0481
443.1534	425.427264	0	0
450.3616	432.347136	5.2414	0.0029
490.3821	470.766816	0.0004	103.6862
506.7302	486.460992	0	1.0418
506.7304	486.461184	0	1.0418
511.9078	491.431488	9.4409	0.0001
511.9307	491.453472	9.4693	0
532.25	510.96	0	0
561.9681	539.489376	0.0005	2.5192
584.5938	561.210048	10.5107	0.0001
584.6023	561.218208	10.5359	0
586.9103	563.433888	0.0064	0
602.2994	578.207424	0.0135	83.7744
627.9271	602.810016	0.6888	0.0938
631.7053	606.437088	0.0003	0
650.7789	624.747744	0	1.5395
650.7789	624.747744	0.0001	1.5395
651.5688	625.506048	4.7191	0.0001
651.6023	625.538208	4.6877	0.0004
690.9744	663.335424	0.4387	321.4272
694.0838	666.320448	0	0.0015
698.5405	670.59888	0	0.001
699.7811	671.789856	0.0001	5.7324
727.9325	698.8152	0.0011	21.5406

727.9333	698.815968	0.0001	21.5401
735.802	706.36992	146.0773	2.2314
763.8062	733.253952	0.0015	814.7804
767.9564	737.238144	56.4339	0.0044
768.0241	737.303136	56.3375	0.016
786.621	755.15616	0.0094	0.001
787.3162	755.823552	79.9393	2.8139
787.9633	756.444768	0.0177	0.0879
787.9634	756.444864	0.0089	0.0882
790.672	759.04512	0.726	200.7272
791.779	760.10784	0.0018	0.002
794.3261	762.553056	0.0004	5.6792
794.3269	762.553824	0.0023	5.6795
796.7407	764.871072	0.0074	0.0002
817.783	785.07168	2.3155	0.0037
818.0102	785.289792	2.4073	0.0204
856.7875	822.516	0.1372	150.5803
864.1961	829.628256	0.1549	0.059
897.251	861.36096	0	4.2468
897.2511	861.361056	0	4.2467
897.311	861.41856	0	0.0001
897.3492	861.455232	0	0
905.7102	869.481792	38.5314	0.0003
905.7222	869.493312	38.5627	0.0007
960.8528	922.418688	0	42.2996
962.5328	924.031488	0.0026	0.0006
962.7145	924.20592	0.0056	1.0535
962.715	924.2064	0.0001	1.0534
962.9611	924.442656	3.1166	1.07
995.2258	955.416768	0	0.0004
995.3152	955.502592	0	0.1689
995.3152	955.502592	0	0.169
995.396	955.58016	0	0
1038.549	997.00704	0.0039	143.8996
1038.7854	997.233984	5.7897	2.6492
1038.8145	997.26192	5.8865	1.4557
1041.8374	1000.163904	0.376	364.6433
1059.6298	1017.244608	0.0006	63.5552
1088.3286	1044.795456	76.4123	0
1088.3305	1044.79728	76.2977	0.0012
1120.2316	1075.422336	0.1334	0.4403
1133.1984	1087.870464	114.378	0.0522
1133.3669	1088.032224	112.6804	0.0029
1141.8943	1096.218528	0	352.1735
1148.3956	1102.459776	186.3642	0.1826
1148.4687	1102.529952	188.4205	0.0231
1155.3755	1109.16048	0.0636	978.9055

1170.342	1123.52832	0.0358	0.7113
1173.1897	1126.262112	0.0001	1913.3079
1196.1875	1148.34	0.0004	399.3595
1200.9731	1152.934176	65.1752	0.0019
1200.9795	1152.94032	65.2112	0.0001
1213.5569	1165.014624	0.0001	1190.1137
1221.3344	1172.481024	4.2101	0.0008
1221.3621	1172.507616	4.2074	0.0004
1222.0661	1173.183456	0.0047	0.0001
1246.4526	1196.594496	0.0004	589.0774
1326.0398	1272.998208	39.3052	0.0395
1326.103	1273.05888	39.1901	0.0149
1330.8961	1277.660256	0.0558	0.0485
1338.3401	1284.806496	0	476.4676
1342.774	1289.06304	0.0001	5315.8283
1361.7638	1307.293248	25.5444	0.0904
1361.8755	1307.40048	25.698	0.7476
1384.0218	1328.660928	239.752	34.7985
1384.085	1328.7216	242.8465	4.4723
1386.8253	1331.352288	4.4348	2084.5852
1394.4144	1338.637824	0.0001	1406.9953
1440.3581	1382.743776	0.0189	469.5702
1455.9728	1397.733888	85.741	0.058
1456.0003	1397.760288	85.7142	0.0903
1468.9882	1410.228672	0.0421	227.1719
1480.8377	1421.604192	0.0002	364.1099
1492.0545	1432.37232	0.0001	1767.2448
1511.6533	1451.187168	35.7428	0.0016
1511.6643	1451.197728	36.0539	0.0028
1516.0762	1455.433152	0.0219	0.0372
1521.4661	1460.607456	0.0024	0.0144
1523.2775	1462.3464	0	177.9418
1523.7387	1462.789152	0.0002	0.0023
1523.7482	1462.798272	0.0023	0.1108
1536.326	1474.87296	71.167	0.3013
1536.5337	1475.072352	70.9605	1.1037
1552.3125	1490.22	0.0555	645.1757
1589.5187	1525.937952	0.0002	17682.1128
1636.6908	1571.223168	0	22.7588
1637.4693	1571.970528	8.7827	0.0024
1637.4837	1571.984352	8.8081	0.0006
1639.4161	1573.839456	0.0016	98.5947
1661.2952	1594.843392	0.0732	0.0194
1662.6221	1596.117216	11.9895	0.0378
1662.6327	1596.127392	11.8941	0.0259
1664.0387	1597.477152	0.0024	37.0498
3188.0264	3060.505344	2.2883	0.0296

3188.0346	3060.513216	7.827	0.007
3188.0386	3060.517056	5.5818	0.9028
3188.0519	3060.529824	0.0097	440.5512
3202.0047	3073.924512	0.1054	762.8622
3202.0249	3073.943904	52.1761	34.1977
3202.0394	3073.957824	54.5067	4.1068
3202.1453	3074.059488	2.7944	668.8083
3217.245	3088.5552	0.1764	1.9149
3217.3681	3088.673376	15.7934	0.0173
3217.3714	3088.676544	15.9862	0.0012
3217.4733	3088.774368	0.0001	352.9635
3220.3462	3091.532352	0.0036	87.1599
3220.4156	3091.598976	69.6282	2.3027
3220.417	3091.60032	69.6376	1.5593
3221.2402	3092.390592	0.1868	1377.6767

[a] : Scaling factor : 0.96

ZnPc-L

Unscaled wavenumbers (cm^{-1})	Scaled wavenumbers[a] (cm^{-1})	Infrared intensity ($km.mol^{-1}$)	Raman activity ($Å^4.amu^{-1}$)
-7.9818[b]	-7.662528[b]	0.0367	5.6296
9.0423	8.680608	0.0615	21.74
14.2018	13.633728	0.0094	7.8574
21.1958	20.347968	0	0.2103
23.0423	22.120608	0.0208	14.7569
26.6995	25.63152	0.0264	4.8293
34.7326	33.343296	0.4594	3.3349
40.2388	38.629248	0.0152	2.4974
60.1484	57.742464	0.0102	0.7407
60.921	58.48416	0.1753	0.0681
62.735	60.2256	0.1562	0.0507
87.0815	83.59824	0.3736	0.3078
103.0635	98.94096	0.0908	2.8293
108.1228	103.797888	0.0212	2.7541
111.5797	107.116512	0.0007	11.2864
119.9831	115.183776	3.3296	0.5181
122.4438	117.546048	3.4983	0.331
125.0573	120.055008	0	0.0003
129.943	124.74528	0.4811	10.4474
133.6589	128.312544	0.238	9.0786
136.539	131.07744	0	8.1618
137.9304	132.413184	28.982	0.0442
157.2734	150.982464	0.0001	16.4086
171.037	164.19552	16.1696	0.162
197.1678	189.281088	0.3257	2.1764
208.4402	200.102592	0.0332	0.3738
210.6262	202.201152	0	0.0052
222.8106	213.898176	0.0317	7.6068
226.1032	217.059072	3.7745	0.0361
231.6155	222.35088	5.1497	0.3189
235.1525	225.7464	0.0006	20.5341
248.1239	238.198944	0.1566	6.6498
249.0882	239.124672	0.0521	7.1737
253.7401	243.590496	0.0437	53.8775
267.9106	257.194176	0	1.0118
275.0845	264.08112	18.0075	4.5106
287.0265	275.54544	0.949	0.3077
287.5309	276.029664	2.3627	0.4903
294.98	283.1808	3.0094	0.9376
299.4896	287.510016	0.0584	1.8455
303.3597	291.225312	3.0566	0.1873
305.1492	292.943232	4.3735	0.1111
353.6329	339.487584	0.4481	0.0364

356.5368	342.275328	0.0699	3.9748
398.0077	382.087392	0.0094	0.0287
400.1671	384.160416	11.9244	0.8588
438.6712	421.124352	0.0272	0.0815
438.7297	421.180512	0.0029	0.0592
439.0187	421.457952	0.0005	0.0423
445.9507	428.112672	0	0.0008
451.1634	433.116864	3.2393	0.1102
489.8024	470.210304	0.0007	96.2954
508.7758	488.424768	1.4703	0.8917
508.8384	488.484864	0.5465	1.2982
510.008	489.60768	3.9997	0.81
510.851	490.41696	9.0308	0.0019
512.4574	491.959104	22.582	2.0462
534.0928	512.729088	0.0091	1.5527
561.0745	538.63152	0.0001	3.9527
567.45	544.752	0.0659	0.2125
581.8514	558.577344	9.2761	0.2535
582.2842	558.992832	9.2231	0.2541
587.8406	564.326976	0.0001	0
594.7397	570.950112	20.3243	7.1268
599.0237	575.062752	1.3905	60.2202
623.5518	598.609728	6.2584	2.6814
627.0447	601.962912	0	0.003
635.4978	610.077888	0	0.0013
647.3778	621.482688	1.0197	0.7658
647.5764	621.673344	7.3321	0.862
648.1467	622.220832	18.862	2.5776
655.8391	629.605536	0.0028	1.4903
656.505	630.2448	0.0358	0.9043
681.6978	654.429888	0.9635	2.4476
693.4262	665.689152	0.0374	273.3655
698.2116	670.283136	0.045	0.7962
701.6552	673.588992	0.0128	11.405
702.5846	674.481216	26.3378	0.2296
710.7948	682.363008	0	0.8469
735.8438	706.410048	0.8929	17.5093
737.0856	707.602176	1.3687	22.0461
738.5163	708.975648	0.0546	16.7167
752.3338	722.240448	215.497	2.7593
762.849	732.33504	0.0008	829.1712
765.1351	734.529696	0.4305	2.4082
765.7138	735.085248	66.3645	0.5027
765.9888	735.349248	65.9205	0.6598
780.0232	748.822272	4.7861	3.302
787.6581	756.151776	0	18.0185
788.3879	756.852384	0.0006	100.1897

789.94	758.3424	3.6956	0.1674
790.1091	758.504736	3.4947	0.043
795.1107	763.306272	20.9697	3.1138
796.8673	764.992608	1.6002	1.3544
798.3301	766.396896	0.4371	6.4608
799.0125	767.052	0.2506	5.4604
799.0183	767.057568	0.0457	1.0287
813.8252	781.272192	1.0953	0.9854
814.0573	781.495008	1.0671	0.8567
832.0349	798.753504	17.5325	7.3818
839.4136	805.837056	53.7545	4.4001
849.8351	815.841696	3.8913	158.9916
863.0022	828.482112	0	0.0024
880.4056	845.189376	10.1325	8.1594
894.3508	858.576768	4.2317	0.4747
896.2179	860.369184	0.1165	2.9081
896.2323	860.383008	0.0838	3.3083
896.3171	860.464416	0.0364	1.2126
896.351	860.49696	0	0.8545
900.8813	864.846048	6.3271	1.8096
904.2531	868.082976	37.1644	0.1206
904.8487	868.654752	35.7899	0.148
959.8946	921.498816	0.0027	0.0958
960.1016	921.697536	0.192	1.0546
960.1254	921.720384	0.0632	1.0172
960.3472	921.933312	2.8112	0.0822
961.8292	923.356032	0.0041	35.0435
968.422	929.68512	0.0583	0.0016
989.1834	949.616064	3.4021	1.1608
992.0017	952.321632	0	0.0232
992.1104	952.425984	0.0004	0.1038
992.164	952.47744	0	0.1024
992.2673	952.576608	0.0005	0.0522
998.408	958.47168	0.2083	0.1254
1038.0637	996.541152	0.005	134.6432
1038.2528	996.722688	7.2744	1.9492
1038.3105	996.77808	7.2676	1.8731
1038.7564	997.206144	3.9168	335.6925
1040.169	998.56224	18.8081	29.3265
1059.4594	1017.081024	14.2993	10.4367
1059.7363	1017.346848	0.5225	43.4984
1060.3903	1017.974688	0.7502	1.8218
1086.5248	1043.063808	91.6037	2.5195
1086.7416	1043.271936	93.6185	2.2979
1099.8854	1055.889984	15.5015	11.4801
1118.9962	1074.236352	0.0001	0.0013
1131.2345	1085.98512	126.5975	2.0874

1132.5396	1087.238016	4.1699	1.2383
1134.0729	1088.709984	95.0678	2.8358
1141.8892	1096.213632	0.0092	303.5669
1146.014	1100.17344	169.1954	4.5129
1146.0967	1100.252832	2.0527	8.866
1146.7892	1100.917632	192.6333	5.704
1152.9312	1106.813952	0.6701	862.3469
1161.2356	1114.786176	22.868	0.8284
1171.921	1125.04416	0.0001	1696.9687
1177.94	1130.8224	0.0006	0.6003
1194.6081	1146.823776	0.8749	310.4366
1199.0912	1151.127552	61.3912	1.2731
1200.0575	1152.0552	65.9992	1.9996
1213.5384	1164.996864	0.0001	1116.4471
1218.0807	1169.357472	1.794	4.7146
1218.4652	1169.726592	1.3828	4.9539
1225.5702	1176.547392	0.0023	0.3513
1238.1358	1188.610368	1.5902	9.5172
1249.1341	1199.168736	0.0123	504.2187
1258.9105	1208.55408	24.5833	12.4745
1308.2828	1255.951488	2.2125	0.5371
1323.4763	1270.537248	32.1467	0.1396
1323.7383	1270.788768	33.3735	0.2149
1329.6931	1276.505376	0.0003	0.2597
1335.4888	1282.069248	0.2049	6.3435
1337.5444	1284.042624	0.0021	433.8328
1346.9845	1293.10512	0.0064	5138.6961
1354.2	1300.032	13.4818	3.1878
1362.438	1307.94048	16.8239	13.261
1362.6643	1308.157728	16.564	13.8157
1383.404	1328.06784	210.0924	4.0015
1383.6408	1328.295168	203.3252	3.7367
1385.5363	1330.114848	24.0705	1951.4597
1390.4877	1334.868192	158.4059	67.0169
1394.3116	1338.539136	0.0001	1437.7889
1394.8408	1339.047168	5.1621	1.176
1433.6653	1376.318688	181.9787	2.2304
1441.0641	1383.421536	17.3263	538.4891
1453.2139	1395.085344	68.5608	2.8137
1453.7206	1395.571776	70.1969	2.0284
1469.2489	1410.478944	0.0226	186.04
1471.997	1413.11712	17.5735	0.0937
1478.1951	1419.067296	0.1164	312.5099
1492.0746	1432.391616	0	1492.1543
1499.0811	1439.117856	27.3915	15.7578
1509.1534	1448.787264	41.8915	0.5211
1509.7258	1449.336768	44.473	0.9423

1514.3367	1453.763232	0.0042	1.9334
1520.0285	1459.22736	0.0007	0.2347
1521.8263	1460.953248	0.0037	177.9027
1521.9947	1461.114912	0.557	1.9533
1522.0521	1461.170016	0.2526	3.189
1536.9851	1475.505696	85.1963	4.0464
1537.5758	1476.072768	72.6098	3.8227
1548.89	1486.9344	0.1992	502.2893
1553.3927	1491.256992	3.8286	65.32
1589.2304	1525.661184	0.0087	15055.6939
1621.4178	1556.561088	2.0103	2.0604
1637.4302	1571.932992	0.0174	65.5194
1638.2925	1572.7608	11.293	2.2917
1638.3083	1572.775968	10.6935	2.5378
1640.2811	1574.669856	1.76	142.6272
1655.3455	1589.13168	2.744	16.9397
1660.8872	1594.451712	0.0006	0.0473
1662.3376	1595.844096	10.9658	0.07
1662.3655	1595.87088	11.2824	0.0242
1663.7024	1597.154304	0.0006	35.6213
1673.132	1606.20672	74.2626	41.5941
1802.9955	1730.87568	401.8118	6.9031
1854.1696	1780.002816	5.6399	36.6808
3097.2578	2973.367488	8.371	68.1297
3149.675	3023.688	0.3281	27.9798
3185.6012	3058.177152	3.6747	0.5714
3185.6177	3058.192992	4.9063	190.9381
3185.7673	3058.336608	4.6518	0.7606
3185.7845	3058.35312	3.6148	240.4461
3199.8723	3071.877408	23.1299	458.0854
3199.9426	3071.944896	47.8215	153.2125
3200.0182	3072.017472	36.6226	295.026
3200.1089	3072.104544	14.0029	557.6112
3213.2461	3084.716256	0.038	9.0533
3213.337	3084.80352	1.3048	36.3377
3215.2056	3086.597376	1.4612	0.165
3215.3333	3086.719968	15.3621	30.4054
3215.348	3086.73408	20.0019	1.3784
3215.4611	3086.842656	0.864	313.9063
3218.4526	3089.714496	23.0923	67.0133
3218.5451	3089.803296	76.7161	44.7717
3218.559	3089.81664	50.837	33.0434
3218.8606	3090.106176	4.0171	1299.7232
3225.7257	3096.696672	2.0742	3.0697
3228.052	3098.92992	0.2218	116.8235
3259.1832	3128.815872	0.0004	76.4215
3278.8801	3147.724896	0.0396	144.3857

[a] : Scaling factor : 0.96

[b] : Based on its low value, this imaginary frequency was ignored.

Water Contact Angle Measurements

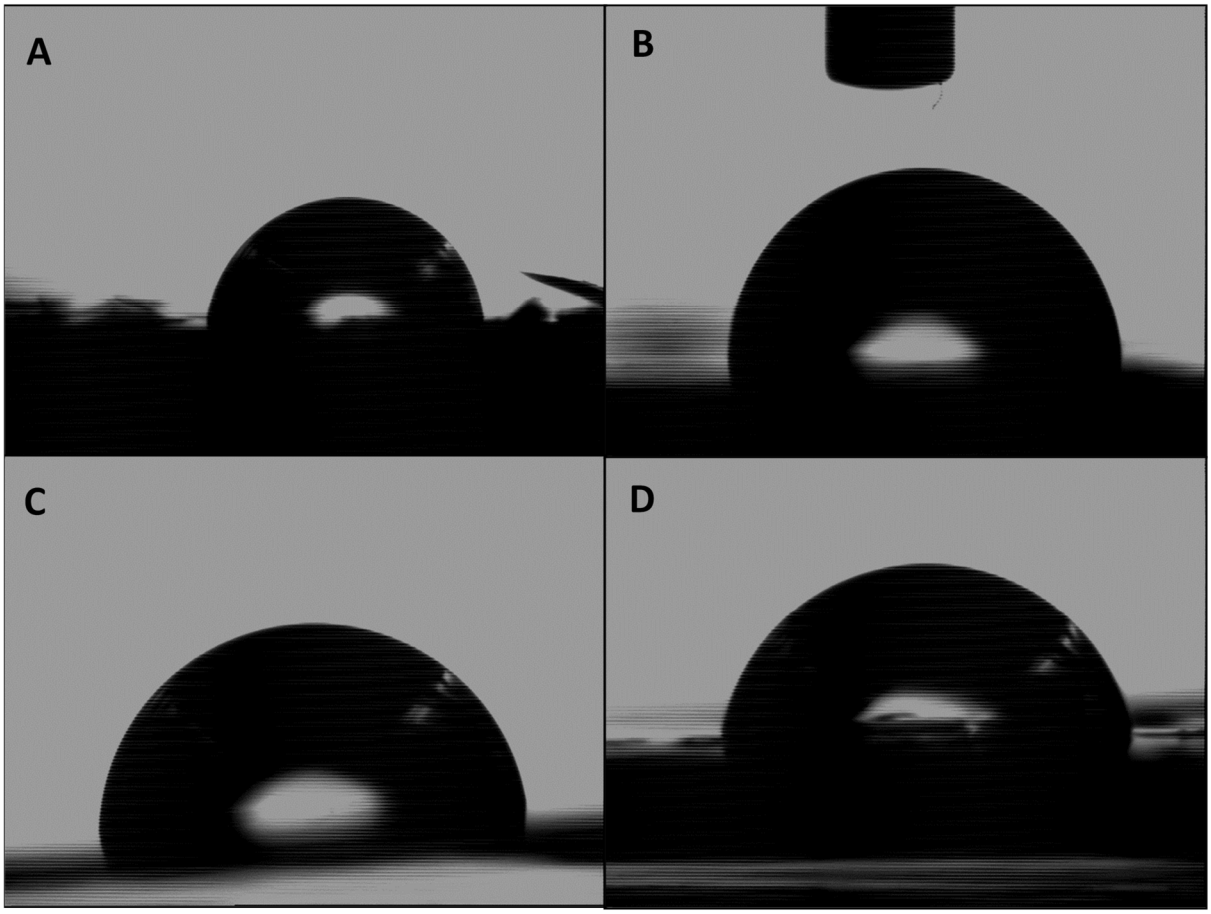


Figure S3 : Contact angle measurement made by depositing a drop of 1 ul of pure water (Millipore grade) on HOPG substrate: A) Raw HOPG; B) HOPG with supramolecular TSB3,5C12 network; C) HOPG with TSB3,5C12 supramolecular network filled with ZnPC; D) HOPG with TSB3,5C12 supramolecular network filled with ZnPc-L.

Substrate,	**Contact angle**
Pure HOPG,	Θ = 84.6° ± 0.8°
HOPG + **TSB3,5-C_{12}**,	Θ = 91.2° ± 1.4°
HOPG + **TSB3,5-C_{12}** + **ZnPc**,	Θ = 85.7 ° ± 1.1°
HOPG + **TSB3,5-C_{12}** + **ZnPc-L**,	Θ = 78.1 ° ± 1.3°

Table S1 – Summary of the results obtained for contact angle measurement of the different substrates

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