SUPPORTING INFORMATION

Low frequency noise in nanoparticle-molecule networks and implications for in-materio reservoir computing.

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NMN fabrication.

*Electrodes on Si/SiO*₂. We used a $\langle 100 \rangle$ oriented silicon wafer covered with a 200 nm thick silicon dioxide thermally grown at 1100 °C during 135 min in a dry oxygen flow (2 L/min) and followed by a postoxidation annealing at 900 °C during 30 min under a nitrogen flow (2 L/min) to reduce the density of defects into the oxide and at the Si/SiO₂ interface. The metal electrodes were fabricated by e-beam lithography. We used a 45 nm-thick PMMA (4% 950 K, diluted with anisole with a 5:3 ratio), with an acceleration voltage of 100 keV and an optimized electron beam dose of 370 μ C/cm² for the writing. After the resist development (MIBK:IPA 1:3 during 1 min and rinsed with IPA), a metallic layer (2 nm of titanium and 12 nm of gold) was deposited by e-beam evaporation followed by

the liftoff process using remover SVCTM14 during 5 h at 80 °C. We obtained well defined 6 coplanar electrodes arranged around a ring with a diameter between 80 to 120 nm.

Synthesis of molecularly functionalized Au NPs and deposition on a substrate. To better control the size of gold nanoparticles (≈10 nm), we decided to prepare oleylamine-coated Au NPs by a phase transfer protocol^{1, 2} from citrate-coated AuNPs instead of the direct reduction^{3, 4} of tetrachloroauric salt with oleylamine (Fig. S1). First of all, a 100 mL aqueous solution of 10 nm citrate-AuNPs was obtained following the Turkevich method.⁵ A solution with 1 mL of tetrachloroauric acid trihydrate HAuCl₄.3H₂O (1%) in 79 mL of deionized water was prepared. Then a 20 mL reducing solution with 4 mL of trisodium citrate dihydrate (1%) and 80 µL of tannic acid (1%) in 16 mL of deionized water was added rapidly to the Au solution under vigorous stirring (important : both solutions were mixed at 60 °C). The mixture was boiled for 10 min before being cooled down to room temperature. A continuous stirring was applied throughout the process. Then, the 100 mL solution of citrate capped NPs was extracted with 20 mL of hexane containing 0.2 mL of oleylamine. After vigorous stirring, in a separatory funnel, the organic phase was isolated and washed twice with deionized water. The dark red suspension was distributed in centrifuge tubes and then added with 50 to 70% ethanol until the beginning of the agglomeration (purple shift). After centrifugation at 7000 rpm for 5 min, the precipitate was washed with absolute ethanol then redispersed in hexane. The washing of the NPs by precipitation with ethanol then redispersion in hexane was repeated twice in order to eliminate the excess of oleylamine. The NPs suspension is stable in hexane or toluene. It is stored in the refrigerator.



Figure S1. Scheme of the NMN synthesis routes. The green arrows stand for ligand exchange in solution, the blue arrows indicate the transfer printing method and the orange one represents the on-surface ligand exchange (see text for details). In the case of POMs, the counterions (3 TBA+ per POM) are omitted for clarity.

The next step is to form a compact 2D network of the NPs at the surface of the Si/SiO₂ substrate with patterned electrodes (Fig. S1, blue arrow). We used the Santhanam⁶ method to form a Langmuir film at the surface of a non-miscible and non-volatile solvent. Water and ethylene glycol meet these criteria but we have obtained better quality films with ethylene glycol. In a crystallizer, we put a pierced Teflon Petri dish (hole diameter: 2 cm) upside down. We add ethylene glycol (EG) until we form a meniscus on the hole and then we spread some drops of the solution of NPs. We protect the assembly by covering with a crystallizer and wait around 10 minutes that the solvent evaporates and the film is self-organized on the EG surface. Then, we used a polydimethylsiloxane (PDMS)

stamp to collect the NP films and transfer it on the surface of the SiO₂/electrode substrate, following the Langmuir–Schaefer technique.⁷ We delicately put the PDMS stamp on the surface of the meniscus, dry the stamp under nitrogen flow and we recover the SiO₂/electrode substrate with this modified stamp. We take it out after a few seconds to be sure that the network of oleylamine-NPs is well transferred and we rinse quickly with ethanol the functionalized substrate. The film peels off easily from the PDMS tab. Then, we check the homogeneity and organization of the film by scanning electron microscopy (SEM), Fig.S2. We clearly observed the deposition of a monolayer of oleylamine-NPs with mainly a roughly hexagonal arrangement of the NPs and an almost homogeneous size of NPs. The zoom images were treated with ImageJ⁸ to give us statistical data of the NP diameter (we used the Feret's diameter) and the inter-nanoparticle distance was calculated with the nearest neighbor distance (NND) ImageJ plugin.



Figure S2. (a-b) Scanning electron microscope images of the oleylamine-NMN at different magnifications (82.06k and 648.56k, respectively). The panel (a) shows the 6 electrodes and the monolayer of NPs, the central ring between the electrode has a diameter of ca. 100 nm. Panel (b) is a zoom near the electrodes. The roughly hexagonal packing of the functionalized NPs is illustrated by the dotted white lines in the panel (b). (c-d) Histograms of the NP diameter and nearest neighbor distance (NND), respectively. The red lines are Gaussian fits, the mean values and standard deviations are given in the figures.

Figure S2 shows the distribution of the diameter of the NPs, the mean diameter is around 7.8 nm. The nearest neighbor distance (NND) is around 1.8 nm. The length of the oleylamine is ca. 2.0 nm⁹ indicating that the ligands are strongly

interdigitated and folded (likely at the double bond) in the gap between two neighboring NPs.

Ligand exchange. The last step is the ligand exchange to replace the capping ligands (citrate or oleylamine) with the thiolated molecules (octanethiol, azobenzene, polyoxometalate), the thiol-ligand exchange was already demonstrated elsewhere.^{10, 11} Transfer of citrate-NPs in organic medium was necessary for the thiolation reaction with octanethiol (Fig. S1). To this end, the 100 mL citrate-NPs solution was centrifuged at 13000 rpm for 30 min to eliminate the maximum of water supernatant. Then NPs were precipitated by the addition of an excess of ethanol and centrifugation at 10000 rpm for 5 min. After removal of the solvent, the black precipitate physisorbed on the centrifugation tube (attention, do not dry the precipitate!) was redispersed in 10 mL of absolute ethanol by sonication, providing a dark blue suspension immediately treated with 100 μL of octanethiol. The solution quickly turns red-purple but the thiolation is continued 24h at RT protected from air and light. The resulting black precipitate was washed 3 times with ethanol at low speed centrifugation (2000 rpm max), then redispersed by sonication in CHCl₃ for the preparation of MNMs.

The same method was used for the synthesis of azobenzene-NPs as already described in a previous work.⁴

We also tried to apply this method to prepare a suspension of POM-NPs in organic medium but it was not possible to obtain NMN films by the Langmuir technique. To get around the problem, for the preparation of POM-NMNs we opted for a ligand exchange method on a preformed NPs network (Fig. S1, orange arrow). To this end, we immersed the oleylamine-NMN substrate (SiO₂ with electrodes) in a 10⁻³ M solution of POM in acetonitrile during 5-10 minutes. Then

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the substrate was rinsed quickly with acetonitrile and it was dried under nitrogen flow.

Figure S3 shows the SEM characterization of the octanethiol-NMNs. The mean NP diameter is still 7.8 nm, but a tail at larger sizes indicates that some NPs are aggregated. The mean NND distance is 1.5 nm which indicates that the C8 alkyl chains (length of ca. 1.3 nm in their all-trans conformation) are strongly interdigitated and/or folded with the presence of gauche defects. We also observe a tail of the NND at larger sizes, which is due to presence of numerous voids in the layer as visible in the SEM images.



Figure S3. (a-b) Scanning electron microscope images of the octanethiol-NMN at different magnifications (132.41k and 279.91k, respectively). The panel (a) shows the 6 electrodes and the monolayer of octanethiol-NPs, the central ring between

the electrode has a diameter of ca. 100 nm. Panel (b) is a zoom near the electrodes. **(c-d)** Histograms of the NP diameter and nearest neighbor distance (NND), respectively. The red lines are Gaussian fits, the mean values and standard deviations are given in the figures.

We prepared two batches of the POM-NMNs, which have a slightly different organization of the nanoparticles (NPs) in the NMN (Fig. S4). For batch 1 the NPs are slightly denser than for the batch 2 (Fig. S4a and S4b, respectively). Figure 1 (main text) and Fig. S4a show the SEM images of the POM-NMNs after the on-surface ligand exchange (batch 1). We still have a 2D monolayer of NPs and the organization of the NPs looks stable after the exchange and we still observed a hexagonal packing. From the image analysis (Fig. S4c), the mean NP diameter is in the range 7-8 nm. The NND is slightly larger and more dispersed for the batch 2 (Fig. S4e and S4f). Compared to the size of the POM molecule (\approx 1.8 nm, see Table 1 main text, or even a bit less since the short alkylthiol legs are flexible), we assume that no more than one layer of POMs is surrounding the NPs and intercalated in the gap between two adjacent NPs.



Figure S4. **(a-b)** Scanning electron microscope images of the POM-NMNs for batches 1 and 2 (magnification 652.75k and 162.96k, respectively). The hexagonal packing of the functionalized NP is illustrated by the dotted white lines in the panel. **(c-d)** Histograms of the NP diameter for the NMNs of batch 1 and batch 2, respectively. **(e-f)** Histograms of the nearest neighbor distance (NND) for

batch 1 and batch 2, respectively. The red lines are Gaussian fits, the mean values and standard deviations are given in the figures.

For the azobenzene-NMN, the mean NP diameter was 9 nm with a mean NND of 4.5 nm as fully characterized in our previous works.^{4, 12}

Estimation of the voltage inside a single AuNP-molecule-AuNP

The voltage across an individual NP–molecules–NP building block junction in the NMNs is roughly approximated by the applied voltage divided by the number of such junctions in series between the PEs (\approx 5 to 15 as estimated from the SEM images for the NMN with a central diameter of \approx 100 nm and depending on whether the PEs are diametrically located of side-by-side). For a crude estimate, we can consider that on average *ca.* one tens of the external applied voltage is sustained by single NP-molecule-NP building block.

In the case of the azobenzene-NMNs (see Fig. 3a in Ref. 12), in the voltage range 8-12 V (voltages at which the LFN behavior of the *trans* azobenzene-NMNs tends to be similar to the one of the *cis* azobenzene-NMNs) and considering an average inter-nanoparticle distance of \approx 4.5 nm (Table 1, Ref. 4), the electric field in an individual NP–azobenzene–NP junction is \approx 1.2-5.3x10⁻² V/Å.

Additional data.



Figure S5. Current-voltage (I-V) curves recorded for several pairs of electrodes (PEs) of the octanethiol-NMN and oleylamine NMN.



Figure S6. Current power spectral density (PSD), $S_l(f)$, versus frequency for the octanethiol-NMN, PE #1, and the two PEs of the oleylamine-NMN, measured at several applied voltages.



Figure S7. Current-voltage traces of the LC POM-NMN (zoom on data from Fig. 3B, main text)





Figure S8. Current power spectral density (PSD), $S_l(f)$, versus frequency for the POM-NMNs (batch 1: PEs #1 and #2; batch 2: PEs #3 to #6) measured at several applied voltages.



Figure S9. (a-b) Current power spectral density (PSD) $S_1(f)$, versus frequency for the two PEs of the POM-NMNs measured at several applied voltages from 0.2 to

1V. (c) Frequency exponent, n, versus the applied voltage. The dashed line is a guide for eyes. (d) Noise power versus the DC current. The dashed lines are a guide for the eyes.



Figure S10. Two sinusoidal signals, signal A at 8.5 Hz and signal B at 18.5 Hz
(peak-to-peak amplitude V_{PP} = 2 V for both) are applied at two electrodes of the POM-NMN. At the other 4 outputs, the currents are measured by a transimpedance amplifier and fed to the dynamic signal analyzer for FFT analysis. The HHG peaks are labeled as Ai (i = 1 for the fundamental, i = n for the nth harmonic, n is an integer) and Bi for harmonics corresponding to the A and B

input signals, respectively. Only the main HHG are shown for illustration. Peaks in between these integer harmonics correspond to interharmonic distortion and intermodulation distortion (see Ref. 12 for details on the method and analysis procedure). The large number of generated harmonics by the NMNs is the fingerprint of its strongly nonlinear response. The HHG spectra are also different for the 4 outputs, indicating the variability of the building blocks and interactions in the NMN.



Figure S11. Noise floor of the setup measured for the two channels (the two trans-impedance amplifiers and the two-channel digital signal analyzer) with the prober tips raised (no sample).

Reservoir computing.

The concept of reservoir computing (RC) has emerged at the beginning of the 2000s with two seminal publications of Jaeger et al.¹³ and Maass et al.¹⁴ RC is a peculiar type of the recurrent neural network and it is appropriate for temporal/ sequential information processing.¹³



Figure S12. Principe scheme of a RC that is made of an input layer, a reservoir and a trained output layer. The reservoir is a randomly interconnected (black lines) network of nodes (blue circles). The transfer functions of the links are characterized by weights W_{res} that are held fixed. Several Xi(t) reservoir outputs are read and weighted (W_i) as a linear combination to generate and output O(t), which is compared to the target Y(t). The error Y(t)-O(t) is minimized by updating the weights W_iusing a learning algorithm.

In the RC approach (Fig. S12), the time-varying input signals I(t) feed a reservoir that is characterized by complex dynamics and highly non-linear properties. The reservoir is composed of nodes (blue circles) and links (black arrows). The signals propagate between nodes that are interconnected by links with random weights W_{res} that are characterized by a large variability of values. The reservoir dynamics and non-linearity generate states X_i(t) that are a function of the inputs I(t), the most recent state X_i(t-1) and the weights W_{res} following:¹³

$$X_{i}(t) = f(I(t) + W_{res}X_{i}(t-1))$$
(S1)

In the reservoir, the input signals are projected into a higher-spatio-dimensional representation space. The signals of some output nodes are read by an output

layer (basically a simple perceptron)¹⁵, where the signals are linearly weighted (W_i) to generate the time series output O(t) according to:

$$O(t) = \sum_{i=1}^{n} W_i X_i(t)$$
(S2)

The output layer is trained to perform a given information processing task by comparing O(t) with the target signal Y(t) and updating the weights W_i with an appropriate learning algorithm. Contrary to multi-layer feed-forward neural networks and/or convolution neural networks where all the hidden layer weights need to be trained and adjusted, RC is a simplified computation system at the hardware level because only the output layer weights W_i must be trained, while the reservoir weights (W_{res}) remain fixed. Thus, the implementation of hardware RC was tested using a variety of physical devices and technologies (see a review in Ref. 16) including nanoscale materials and devices (see a specific review in Ref. 17). One of the mandatory conditions for an efficient RC is a large variability of the W_{res} values.^{13, 14, 16, 18} Similarly the topology in the reservoir is fixed and random, and the transfer function of the links and nodes in the reservoir has to be strongly non-linear with a complex dynamic behavior.¹⁸⁻²⁰ Note that the output layer can be implemented physically or most of the time by a software algorithm. In the present case, only the reservoir layer has been implemented, the nodes are the gold NPs and the links are the molecules connecting neighboring NPs.

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