Pyroelectric Tweezers for Handling Liquid Unit Volumes

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Liquids are the primary environments in which chemical, physical, and biological processes occur. Considering a liquid bridge as liquid unit volume (LUV) element, it is highly desirable to develop reliable tools for handling such volumes. Herein, a sort of intelligent microfluidic platform based on the pyroelectric-electrohydrodynamics (EHD) is shown for manipulating liquid bridges and thus performing multiple functions in a flexible and simple way. Several basic operations with liquid bridges using an EHD-pin matrix based on the pyroelectric effect engineered in ferroelectric crystals are demonstrated. By activating pyro-EHD effect in predetermined positions (pins of the array), the locomotion and handling of single or multiple LUVs simultaneously are controlled. In particular, multiple operations such as lift, displacement, mixing, stretching, and carrying vector for microparticles, are shown. These tweezers based on a pyro-EHD matrix can open the route for a multipurpose platform driven by physical intelligence and can be used for driving locomotion and operate manifolds functionalities in many areas of science and technology at microscale as well as nanoscale with advantages to be activated by the sole thermal stimulus, controlled remotely, and in noncontact mode.

1. Introduction

There is a lot of increasing interest in designing innovative methods for handling and manipulating liquid and solid objects with good control and high precision. To meet this specific demand, it is automatic to think about the use of robots, but they usually present very complex architecture and expensive motion-control systems. In particular, most robots are made of rigid components, becoming monolithic structures, not friendly in close contact with fragile objects and unable to self-adapt to various configurations.[1] Their planning and fabrication process are often complicated, inhibiting miniaturization, and constraining the device to a single defined behavior. In fact, their movement could be controlled either by chemical reactions[2] or by direct manipulation using torques or forces applied by external magnetic fields[3–5] or electric field.[6] Alternatively, to preserve the chance to self-adapt, flexible materials could be embedded.[7,8] Following these guidelines, soft-matter engineering is reaching significant breakthroughs in emerging classes of intelligent systems provided with flexible actuation, sensitivity, sporting styles, and biomimetic functionality. Flexible or elastomeric materials could serve as building elements for the fabrication of smart device engineered for unstructured environments, such as the human body, interaction with soft objects, and other natural environments. Hydrogels,[9] liquid-crystal elastomers (LCEs), liquid metal, and shape memory alloys/polymers,[10–12] exhibiting stimuli responsive behaviors, could offer a potential strategy for the fabrication of advanced totally biomimetic self-adaptable systems.[13] Until now, soft-matter engineering has been extensively explored for the fabrication of intelligent systems but problems related to the system management and the continuous demand of device miniaturization, where length scale shrinks, still remain unsolved. The actuation of these existing systems generally relies on applying external magnetic,[14] electric,[6] or optical[15] fields globally over the entire workspace. In particular, in case of liquid manipulation, electro-wetting (EW), and digital microfluidic have been one of the most widely used solution for manipulating tiny amount of liquids on surface.[16–18] Starting from the discussion of the dynamics of EW, new strategies for the automation and integration of fundamental fluidic operations have been proposed for various commercial applications (display technology, fiber optics, biotechnology, biochemical testing, etc.).[19–21] The demanding interest for microfluidic lab on chip systems, especially in a point of care setting, is growing up and focused toward simpler, mass production, and less-expensive solutions, looking in particular toward innovative telemedicine applications. As alternative activation and controlling systems, perspective results have been recorded using optical trapping, where light is used for the manipulation of the matter. In fact, during the years, different fields of technological and biological applications have found in the optical tweezers, a revolutionary method for safe and no contact manipulation of particles, cells, and DNA[22] More
in details, optoelectronic photovoltaic tweezers (PVT), based on the use of ferroelectric crystals (i.e., lithium niobate [LN]), have recently proposed advantages over the conventional optoelectronic technique, ability to keep their manipulation properties on and active, even after the illumination period. The PVT could be used for the manipulation of electrically charged as well as neutral particles, biological materials, and samples more in general for biotechnological applications.\textsuperscript{23} The manipulation of liquids has been also proved by controlling the dielectrophoretic (DEP) behavior of microdroplets sandwiched between parallel LN Fe-doped crystals, where the incident illumination pattern could be transformed into electric field distribution. In this condition, microdroplets can be step-moved, deformed, patterned,\textsuperscript{24} or split in case of antisymmetrical-sandwiched FeLN structures at very small distance (about 20 μm).\textsuperscript{25,26} Unfortunately, the double LN structure is costly and difficult to be fabricated for lab on chip device, an alternative solution has been recently proposed using the PVT for guiding, trapping, merging, and splitting of water drops inside a nonpolar liquid medium.\textsuperscript{27} In this case, the mismatch of different medium still represents a limit for the functionality of the manipulation systems, and to overcome this issue, horizontal liquid bridges have been extensively studied from a theoretical point of view,\textsuperscript{28} whereas vertical liquid bridges have been very recently explored for transferring liquid volumes in air between two vertically separating flat surfaces.\textsuperscript{29,30} In the manipulation context of liquid and micro-objects, an important role has been recently played by the pyroelectric effect (PYT), already exploited for high-resolution inkjet printing and manipulation of polymers.\textsuperscript{31–33} Herein, we propose, for the first time, a tweezer system based on the PYT for miniaturized actuation, accurate remote locomotion, and lift against the force of gravity of liquids volumes and micro-objects by thermal stimulus. An electric field generated by temperature gradients is used to move small volumes of liquids and polymer drops, representing a new paradigm for miniaturized and digital microfluidics. The manipulation of liquid unit volumes (LUVs) works at room temperature, in air, in three dimensions and using a working distance bigger with respect to PVT systems, allowing demand driving and control of liquid bridges. Managing the on/off activation system of the pyro-EHD effect allows controlling a fast response for moving LUVs. The locomotion of LUV is influenced by the design chosen for the activation of the pyro-electric field and by the interaction with the environment. Directional locomotion, lift, mixing, jumping, and stretching are possible actuating functions that we demonstrate herein. In the following, a complete exploration of the opportunities and working conditions of a multipurpose platform guided by a physical intelligence is proposed and analyzed point by point, including the functional-ization of single drop or multiple LUVs at the same time.

2. Experimental Section

2.1. Materials

Z-cut LN crystals, which were polished both sides with 500 μm thick, were purchased from Crystal Technology, Inc. and cleaned with acetone and 2-propanol. Mineral oil and liquid crystals (LCs) (4’-hexyl-4-biphenylcarbonitrile) were purchased by Aldrich and used without further purification. The fluorophores were CdS nanorods with photoluminescence peaks at 450–500 nm for the blue one and 570–610 for the yellow, they were purchased by Sigma-Aldrich in powder and used to color different liquid drops.

2.2. Microheaters Fabrication

The samples were fabricated by integrating a resistive coil made of titanium film on a LN crystal. The coil was designed in a double meander shape to produce very localized heating by pyro-EHD effect using low circulating current. The fabrication was based on standard optical photolithography for pattern definition and thin-film titanium deposition via direct current (DC) sputtering in ultrahigh vacuum system. A lift off procedure defined that the final geometry consisted of an array of 3 × 3 square meanders with each having a side of 1 mm and arranged at distance of 4 mm each other. The single element consisted of a wrapped coil having both linewidth and interspacing of 50 μm. The titanium thickness was 250 nm, and the resistance, at room temperature, of each coil was 2.8 kΩ. Therefore, a current of 10 mA produced, by Joule effect, a dissipative power of 280 mW in each coil.\textsuperscript{34}

2.3. Electronic Controller

The electronic control of the microheaters (μHs) was composed by an Arduino UNO board and a custom-made control circuit. The control circuit is shown in Figure 1. The Arduino board was programmed to be controlled by a custom-made graphical interface on a personal computer using processing, an opensource graphical library and integrated development environment (IDE). The graphic interface was used to select the desired μHs to switch on and send the correct signal to the Arduino board. The Arduino board controlled a shift register directly for which the output pins were connected to five optocouplers to decouple the Arduino board to the rest of the circuit. The opto-coupler, powered by a 5 V regulator (itself powered by the external voltage generator), controlled the base of five NPN bipolar junction transistors that were responsible to drive the current toward the μHs. To avoid an excessive current to flow through the μH, a resistor was positioned in series to the output of the external power supply.

2.4. Experimental Setup

The LN crystal with the titanium μHs was positioned on a microscope glass cover slip (thickness 150 μm) to provide a physical support to it. The cover slip was clamped on a movable sustain and accurately adjusted parallel to a glass slide on which the oil drop was positioned (Figure 1). A single-axis translator, which could move in the z direction, supported the glass slide. In this way, the small oil drop could be slowly approached toward the upper cover slip. The oil drop formed a liquid bridge between the support glass slide and the cover slip, as shown in Figure 1a,b. After the formation of the liquid bridge, the liquid was moved activating the electric voltage on a specific μH using the custom-made software and the Arduino UNO board (Figure 1c). The device was mounted in a 3D-printed support.
as shown in Figure 1d–e. The supporting slide could be easily replaced, whereas the LN crystal with the titanium μH could be reused indefinitely. The typical volume of the starting drop was in the range of $30 < V_d < 80 \mu L$, whereas the drop diameter ranged between 2 and 4 mm. The working distance between the glass and the supporting slide of the LN crystal was in the range between 2 and 6 mm. The typical working distances discussed in the experiments in the following were much larger than the ones reported in similar experiment of liquid manipulation (i.e., tens of micrometers), providing the unique possibility of controlling and tweezeing millimeter-sized objects. The experimental parameters discussed (drop volume, radii, working distance, electrode dimension and electrode pitch) were strictly correlated, also depending on the surface coating of the substrates. We started fixing the dimension of the μHs, and depositing a liquid drop that would be able to create a liquid bridge containing the μH in the circular base (as shown in the Supporting Information, movies).

### 2.5. Liquid Actuation

Until now, interesting and well-established techniques were adopted to manipulate liquid droplets. These techniques relied on the forces acting on dielectric fluids when immersed in a high-intensity electric field, and the motion of the droplets was actuated by precisely controlling the voltage between two adjacent electrodes. In particular, these forces could be divided in two different contributions: the EW effect and the DEP forces. Commonly, EW and DEP devices for manipulation of fluid relied on the use of complex and bulky device and expensive and risky external generators for the production of high-intensity electric fields. In our experiments, we proposed the use of high-intensity electric fields induced by pyroelectric crystals. Pyroelectricity is the property of some materials to generate an electric potential difference between two opposite sides, of a crystalline phase, due to a change of temperature. To be pyroelectric, the crystal lattice of the material had to show some specific characteristic of symmetry (i.e., not having a center of symmetry) and possess a spontaneous polarization of the unit cell. On heating this dipole changes, its starting value (due to displacement of the atoms and thermal expansion of the lattice) and, if all the unit cells were directed toward the same direction (i.e., the crystal has a non-zero average direction of alignment of the unit cells), the sum of all these dipole variations generated an elevated electric potential difference between two opposite faces. The LN crystal was a ferroelectric material which exhibits pyroelectricity at room temperature. Without thermal stimulus, the spontaneous polarization of the crystal was fully compensated by the external screening charges so that no electric field existed, and the LN crystal was in equilibrium. 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actuation.[35] The changes of the spontaneous polarization vector $P_i$ is governed by a simple equation $\Delta P_i = p_i \Delta T$, where $p_i$ is the pyroelectric coefficient and $\Delta T$ is the temperature variation.

In this work, a PYT device was created by patterning metal $\mu$Hs (Section 2.2) directly onto the pyroelectric LN substrate. The heaters were connected to an external low-tension generator used just for inducing a local heating of the crystal. On heating (about 80–100 °C), a localized electric potential of the order of magnitude of hundreds of volts was generated, and an EHD force was exerted over the dielectric liquid droplet. The activation of the pyro-EHD field was totally safe and easy to use for the final user. In fact, the user could switch on and off the pyro-EHD effect simply using a programmed interface and clicking by mouse on the area of interest, without direct and dangerous interaction with external voltage generators. With immediate effect after the clicking, a localized pyro-EHD effect was seen and could be used to manage LUVs and guide liquid locomotion. By implementing an array of $\mu$Hs on the surface of the crystal, the final user could select the $\mu$Hs using an external controller, and in real time, manage the direction of the motion of multiple droplets along several trajectories. The final device resulted flat, light, and could be easily integrated in lab on chip and microfluidic platform.

2.6. Simulations

The pyroelectric field generated by the LN was calculated using a finite element method (FEM) commercial software (COMSOL Multiphysics). The electrical current flowing into the $\mu$Hs was simulated, in stationary condition, using the thin-layer approximation module coupled with a thermal generation due to Joule effect. Using a Multiphysics interface, the temperature profile on the thin layer and, due to thermal diffusion, in the LN crystal was also calculated. As final step, the temperature profile was coupled to the alternating current (AC)/DC module, and the pyroelectric field was estimated. The calculation of the pyroelectric field was carried out (as already showed in previous works[36–39]) by imposing a remnant electric displacement proportional to the temperature difference (with respect to the ambient temperature) and to the pyroelectric coefficient of the LN ($p = -4 \times 10^{-5} \text{ CK}^{-1} \text{ m}^2$). Figure 2a shows the calculated electric potential on the surface of the LN crystal due to the electrical Joule heating of the $\mu$H. The correlated electric field lines are shown in Figure 2b and are clearly directed toward the center of the $\mu$H (i.e., from the lowest electric potential toward the highest). The electrothermal behavior of the device is shown in Figure 2c. The higher temperature reached by the $\mu$H for an external imposed potential...
of 16 V is 120 °C. This value was confirmed by the infrared (IR) data acquired using a thermocamera (Experimental details reported in Section 2.7), as shown in Figure 2d and by the curves in Figure 2e.

2.7. Thermal Analysis

An IR thermocamera (Infra Tech VarioCam with 640 × 480 pixel) was used to acquire IR emission from the μHs. To considering the difference in emissivity between the LN crystal and the Ti electrodes, we performed a calibration procedure. The LN crystal with the Ti μHs features was laid on a thermal plate positioned vertically in front of the thermocamera. The plate was turned on and set to different temperatures, from 40 to 100 °C with an incremental step of 10 °C. The system was kept at constant temperature for 2 min to reach thermal equilibrium before acquiring the IR image. Figure 3a shows how at constant temperature different values were measured. From these data, considering the Stefan–Boltzmann equation

\[ E = \varepsilon \sigma T^4 \]  

That states that the radiative energy emitted by a not perfect black body is proportional to the fourth power of its temperature, we can derive the relation between the measured temperature and the real temperature of the body

\[ E_{\text{measured}} = E_{\text{real}} - E_{\text{ambient}} \]  

\[ \varepsilon_a \sigma T_m^4 - (1 - \varepsilon_a)\sigma T_a^4 = \varepsilon \sigma T_r^4 - (1 - \varepsilon)\sigma T_a^4 \]  

where \( \sigma \) is the Stefan–Boltzmann constant; \( T_m, T_r, \) and \( T_a \) are, respectively, the measured, the real, and the ambient temperatures (all expressed in kelvin); \( \varepsilon_a \) is the value of emissivity used for the acquisition of the image (in this case 0.95), and

**Figure 3.** a) Temperature profile for the device during the calibration procedure for a line intersecting the different parts of the device (the μHs labeled “LN + Ti”; the pads labeled “Ti”; the crystal labeled “LN”; the temperature reference labeled “Ref.”); b) emissivity profiles dependence from the temperature calculated using Equation (4); c) variation of the emissivity with the temperature for the different zones of the device; d) calibration curves used to estimate the real temperature of the device depending on the material.
$\varepsilon_r$ is the real emissivity of the body (that we want to estimate). From Equation (3), we can deduce that

$$\varepsilon_r = \frac{\varepsilon_a (T_4^h + T_4^a)}{T_4^r + T_4^a}$$

(4)

Figure 3b,c shows the different values of the emissivity for the different parts of the device depending on the property of the material. From these data, we calculated the calibration curve shown in Figure 3d.

3. LUV Manipulation by PYT

3.1. PYT—Pyroelectric Tweezer

As explained in Section 2.4, a small drop of mineral oil was deposited over a glass slide connected to a linear translator that could move in the z direction. Facing the sessile oil drop, a glass cover slip was adjusted parallel to the base glass slide. The LN crystal was positioned over the cover slip, and the titanium $\mu$Hs were connected to the electronic control system. At time zero of the experiment, the LN crystal was at room temperature, and all the charges were in equilibrium. After this alignment step, the liquid drop was raised toward the glass slide to form a liquid bridge, used as model of LUV, between the two surfaces. The lift of the liquid toward the upper surface, required for the formation of the liquid bridge, was induced by the activation of the pyroelectric field in correspondence of a single $\mu$H above the oil drop (Figure 4a). During the experiment, we followed the movement of the drop using a camera positioned above the LN crystal. At this point, the closest $\mu$H to the liquid bridge was activated (using the graphical interface) to attract the LUV and move it toward adjacent position. The current induced by the potential difference between the two electrodes of the $\mu$H generated enough heat, due to the Joule effect, causing a local raise in the temperature of the LN, see Movie S1, Supporting Information. This was also shown in the simulation in Figure 2a,b. The typical activation energy required for the manipulation of the droplet was about 16 V, corresponding to a local increase in the temperature from ambient to around 80–100 °C (Figure 2e). This value was found to be the optimal minimum potential and was maintained constant for all the experiments.

The heat produced by the Joule effect, increases the temperature of the LN crystal, leading to the generation of a strong pyroelectric field. As shown in Figure 2b, the electric field lines generated a strong nonuniform field below the LN crystal. As shown in previous studies,[40] dielectric liquids are subjected

![Figure 4. Schematic mechanism of the movement of the drop under the pyroelectric field. a) The oil drop is captured by the electric field (green lines) generated by the crystal in correspondence of an active $\mu$H. The drop deforms first in a Taylor cone and then liquid bridge is established between the plates. b) The first $\mu$H (left side) is turned on and the liquid bridge is established once the electric field is on. c) The switching off of the left $\mu$H and the contemporary activation of the adjacent $\mu$H (right side) attracts the drop in a different location due to EHD forces. The figure reports the microscope upper view, where the presence of the liquid bridge is proved by the circular profile visible under the $\mu$H, and the schematic representation of the side view to better explain the phenomenon.](image-url)
to a force, when immersed in a nonuniform electric field, directed toward (positive DEP) or outward (negative DEP) the regions of higher intensity, depending on the relative values of the dielectric constants (i.e., the Clausius–Mossotti coefficient) of the particle and of the surrounding media. If the liquid is immersed in air, the DEP is always positive ($\varepsilon \approx 1$). For this reason, the LUV was attracted toward the active $\mu$H. Sequentially the other $\mu$H were activated one by one to move the liquid across the crystal surface. Whenever a new $\mu$H was switched on, the previous was turned off, to maximize the attraction to the new position (Figures 4b,c). This process could be repeated indefinitely. As the system is strongly susceptible to small imperfections (e.g., alignment of the substrates, dust on the glass slide) the time taken by a drop to “jump” from one position to the next one varied from 1–2 s to almost 10 s. The final position of the geometrical center of the LUV is not always perfectly aligned with the geometrical center of the arrival $\mu$H. This misalignment can be related to the decrease in the net force acting on the LUV as a portion of its volume passes over the $\mu$H. Because the positive DEP force is always directed toward the region of highest electric field intensity, the parts of the LUV on the two sides of the $\mu$H are subjected to forces with opposite directions. For this reason, the DEP force is overcome by other forces (e.g., interfacial forces), during the LUV motion, before its geometrical center reaches the center of the $\mu$H. Also the nature of the substrates plays a clear role in the movement of the liquid bridges. The alteration of the wettability of the glass (for example, using a fluorinated silane treatment) can improve or reduce the smoothness of the movement. To demonstrate the principle of operation of the PYT and maintain the easiest configuration, all the experiments were conducted on simple glass, without further treatments of the surfaces, except for cleaning with ethanol to remove residual dust and oil. For future applications, where a fast response could be required, or for dispensing different materials on alternative substrate, surface treatment could be considered and implemented.

### 3.2. Liquid/Solid Manipulation

In the following section, the liquid locomotion was implemented by the PYT in air, at room temperature, with remote control, and at a working distance of tens of mm. In particular, because of this working distance, the manipulation of LUV could be combined also with the handling of solid millimeter-sized object, which is otherwise difficult to be handled in air using the conventional microfluidic platform. LUV can be used as a sort of a carrying vector for transferring and manipulating solid particles embedded in the LUV itself. In such a way, the solid particles can be transported easily. In fact, the LUV becomes a sort of liquid tweezers for manipulating particles embedded therein. This is quite challenging as the manipulation of very small objects is usually very difficult due to the propensity of such materials to accumulate small electrical charges. These charges are accumulated during each friction with other surfaces due to triboelectricity. Often the triboelectric charge causes a fast and unpredictable motion of the microparticle, and for this reason, a single macrosphere could not be easily controlled using directly the pyroelectric field generated by LN. The inclusion of the object inside the liquid bridge made of mineral oil ($V = 40 \mu$L) represented a good alternative for manipulating particles (Figure 5). Figure 5 shows a solid microsphere used for the experiments in conjunction with the LUVs. The sphere (radii 500 $\mu$m) was attracted under the $\mu$H activated using the graphical interface ($\mu$H ON), whereas the liquid bridge was placed under a second $\mu$H turned off ($\mu$H OFF). Then the liquid bridge (LUV) was moved toward the sphere. The movement was controlled by the switching on and off adjacent $\mu$Hs, up to addressing the sphere into the desired position.

Once the LUV reached the sphere, it embraced it all around leaving the sphere suspended in the oil. Now the liquid could be used as a carrying vector and then moving it along a desired path by controlling the sequence of activation of adjacent $\mu$Hs in pyro-EHD microfluidic platform. Using a LUV as liquid container, the surface tension (mineral oil surface tension $\approx 30 \text{ mN m}^{-1}$) will provide enough energy to constrain the particles. Even in case, the electrical charges accumulated by the particles cause their fast and chaotic motion, and they remain inside the LUV, they cannot escape because of its surface energy and thus can be dragged around with the LUV. In other experiment, we could use a LUV made of a homogenous dispersion of microparticles in a liquid solution. In this latter case, the immersion of a sphere in the liquid could be used as an alternative way of a double effect process where the motion of the macro-object could be combined with the functionalization of its external surface. Movie S2, Supporting Information, shows
the top view of the motion process in real time, the oil used for
the experiment was transparent, and it is possible to track the
position of the ball combined with the movement of the liquid
step by step. The guided locomotion could work even when the
LUV enwraps more than one sphere (a black and a transparent
one), as shown in Movie S3, Supporting Information. The LUV
 locomotion is combined with the continuous mixing process due
to the relative motion of the microsphere. The LUV locomotion
could be affected by the presence of single or multiple spheres,
depending on the physical properties of the material used for the
experiments. For future application, surface treatment could be
applied and investigated to the microsphere or different materi-
als either for embedding or for pinning up/down the sphere
at the liquid/air interface. Additional experiments will be also
necessary for defining the way in which the presence of solid
objects could affect the simultaneous locomotion of liquid and
solid objects.

3.3. Merging of Two Homogenous LUVs

The manipulation of LUV in conjunction with solid objects was
proved in the earlier sections. A single LUV was moved along the
desired path using a step-by-step procedure but, the process of
noncontact liquid manipulation could work even with two or
more LUVs simultaneously. As further degree of flexibility,
the LUVs can be made of the same liquid and/or different liquids
as shown in the following paragraphs. Starting from two oil
UVs (mineral oil \( V_1 \approx 40 \mu\text{L}, V_2 \approx 60 \mu\text{L} \)) activated by two sepa-
rated \( \mu\text{Hs} \) on the central row of the matrix used for the experi-
ment, we moved simultaneously the two LUVs by switching
on the \( \mu\text{Hs} \) in a clockwise and symmetrical direction, ending
their walk at the center of the matrix. As final step of the remote
operation, the two LUVs merged in a single LUV, as shown in
the Movie S4, Supporting Information. The proof of principle
demonstrated for two oil LUVs could be used for more than
two starting LUVs, depending on the dimension of the matrix
and on the period used for the array.

3.4. Multiple LUVs Mixing

The same approach could be used for the smart manipulation of
multiple and different LUVs. To show this functionality, two
UVs of oil were colored with two distinct colors: blue and
light orange (see Section 2 for details on the solutions). The
starting LUVs were positioned in correspondence of two
different \( \mu\text{Hs} \) (Figure 6a) in two adjacent rows (mineral oil
\( V_1 = 40 \mu\text{L}, V_2 = 60 \mu\text{L} \)). Two liquid bridges were activated by
switching on two \( \mu\text{Hs} \) simultaneously. In this way, both LUVs
resulted to be anchored in their starting positions. As previously
demonstrated, each LUV can be manipulated and moved individ-
ually by coordinating the activation and deactivation of the \( \mu\text{Hs} \).

As shown in Figure 6a–d, the blue LUV could move toward the
light-orange one by following the activation sequence of the \( \mu\text{Hs} \).
To better explain the path of the LUVs, we circled the \( \mu\text{H} \) acti-
vated (\( \mu\text{H} \) ON) in red and used dotted yellow arrows pointing
at the next position. The LUV passed under three \( \mu\text{Hs} \) before
reaching the final position. Once the blue LUV reached the
light-orange one, they mixed resulting in a single light-yellow
drop. This mechanism can be used to manipulate different
liquids and mix them in a specific location in a contact free
modality. In principle, if the two components of the two
UVs can chemically react with each other when mixed, it would
be possible to control, on a lab-on-chip device, the location of
the reaction between two reactants. The proof of principle of
controlling simultaneously the movement of different liquids
and solutions represented the starting point for remote control
in more complex microfluidic and lab-on-chip devices and could
open new routes for the transport and manipulation of cells.

3.5. Shaping the LUV

In addition to the already illustrated and discussed functionali-

ties, we also easily control the shape of the liquid bridge by sim-
ply adding inside the starting reservoir a microsphere (Figure 7).
At the beginning of the experiment, the sphere is located at the
center of the LUV (mineral oil \( V = 1 \text{mL} \)), and then we sequen-
tially activated the \( \mu\text{Hs} \) positioned around the central sphere
(radius 500 \( \mu\text{m} \)) in a clockwise direction. As soon as the
first \( \mu\text{H} \) was activated, the sphere moved toward it and was
trapped by the electric field generated in correspondence of
the \( \mu\text{H} \). The reservoir, due to the movement of the sphere,
stretched along the same direction and changed its initial shape.
Changing the position of the sphere allowed us to modify the
shape of the starting LUV. The aforementioned experiment
represents the elementary functionality but adding more than
one sphere, and controlling the experimental parameters, we

![Figure 6. Selected frames from Movie S5, Supporting Information, showing the controlled transport and merging of two different liquid bridges, made of different colors: blue and orange. The blue liquid bridge is moved toward the orange one by progressive switching of adjacent \( \mu\text{Hs} \), the yellow arrows indicate the direction of the movement, and the red circle enhances the activated \( \mu\text{H} \). a) The blue liquid bridge is moved toward the underlying \( \mu\text{H} \) and b) then moved to the adjacent one. c) The orange liquid bridge remained in the starting position, whereas the blue one is attracted toward it by the activation of the corresponding heater. d) Once the blue drop reached the orange one, they are mixed, resulting in a single light-yellow drop (dotted red circle). (Yellow scale bar 2 cm).](image-url)
can provide multiple input signals and control complex change in the LUV shape.

3.6. Liquid Crystal

The manipulation of small drops of nematic LCs leads to a very interesting behavior (1-(trans-4-hexylcyclohexyl)-4-isothiocyanato-benzene, LC (nematic), 99% Sigma Aldrich). At the beginning of the formation of the liquid bridge, the temperature of the LC was below the nematic transition temperature ($\approx$40°C) and the liquid appeared “cloudy”. As the nematic phase led to a very intense scattering of the light, the LUV appears colored when illuminated with a blue light ($V_{lc} = 40 \mu L$) (Figure 8a). By switching on and off the $\mu$Hs, the LUV could be moved between neighboring positions similar to the oil drops, we have already described but, in this case, the raise in the temperature showed a secondary effect. As the temperature of the LN increased, the LC drop was heated up. When the temperature of the liquid exceeded the isotropic transition temperature, the LUV became clear because the scattering centers of the LC nematic phase vanished (Figure 8b). In our experiment, the gradient temperature applied for the liquid locomotion was the same as the one required for the phase transition. Using a LC with a higher isotropization temperature, it should be possible to activate the $\mu$Hs with two different current densities to switch between two operative modalities, depending on the temperature reached: LC-locomotion and LC-phase transition. Moreover, during the LUV locomotion, it was possible to observe the simultaneous generation of small liquid droplets. The little droplets were ejected from the upper volume of the liquid column and were collected on the glass slide supporting the $\mu$Hs, eventually collapsing each other. In case of LC locomotion, the generation of femtoliter droplets was a consequence of the dispensing due to the activation of the PYT.\(^{[35]}\) The manipulation property raised a strong attention in microfluidic as recently demonstrated in case of water by photovoltaic fields,\(^{[27]}\) for this reason, it would be interesting, in the future, to combine the locomotion of liquid volume with the dispensing of femtoliter drops for personalized functionalization of surfaces.

4. Conclusions

In this work, we have shown that a LN crystal functionalized with titanium $\mu$Hs could be used to manipulate liquid bridges as unit volumes, i.e., LUV. Handling LUVs by this sort of intelligent platform allows to manipulate micro-object embedded in the LUV, such as solids microspheres. We demonstrated that once the LUV was attracted, its locomotion along a desired path could be controlled immediately and in a very easy way through a pyro-EHD matrix. Multiple LUVs can be dragged over the surface, moved simultaneously, and mixed in case of need in a sort of multipurpose platform driven by a physical intelligence.

**Figure 8.** Selected frames extracted from Movie S6, Supporting Information, showing the comparison between a) the opaque scattering phase of the LC and b) the transparent isotropic phase controlled by the temperature variation of the substrate. (Yellow scale bar 2 cm).
Small particles can be moved using the liquid bridges as carrying vectors, thus exploiting the surface tension of the liquid as a constraint to overcome the electrical forces acting on small particles electrically charged. More in general, the proposed intelligent handling microfluidic pyro-EHD platform is also suitable for the manipulation, transport, lift, stretching, mixing, and release of micro-objects, such as spheres. All the demonstrated functions are illustrated by several movies recorded during the experiments. Further study of liquid bridges would improve a number of EHD-based technologies such as ink-jet printing, pyro-EHD printing, micromaterial and nanomaterial processing, drug delivery, biomedical applications, and cell manipulation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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electrohydrodynamics, handling liquid unit volumes, liquid tweezers, locomotion, liquid manipulation, pyroelectric effects

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[1] G. M. Whitesides, Angew. Chem. Int. Ed. 2018, 57, 4258.
[2] X. Fan, J. Y. Chung, Y. X. Lim, Z. Li, X. J. Loh, ACS Appl. Mater. Interfaces 2016, 8, 33351.
[3] R. M. Erb, J. S. Sander, R. Grisch, A. R. Studart, Nat. Commun. 2013, 4, 1.
[4] C. Liu, H. Qin, P. T. Mather, J. Mater. Chem. 2007, 17, 1543.
[5] Y. S. Zhang, A. Khademhosseini, Science 2017, 356, eaaf3627.
[6] B. R. Donald, C. G. Levey, C. D. McGray, I. Paprotny, D. Rus, J. Microelectromech. Syst. 2006, 15, 1.
[7] Z. Wei, Z. Jia, J. Athas, C. Wang, S. R. Raghavan, T. Li, Z. Nie, Soft Matter 2014, 10, 8157.
[8] S.-J. Jeon, A. W. Hauser, R. C. Hayward, Acc. Chem. Res. 2017, 50, 161.
[9] A. W. Hauser, A. A. Evans, J.-H. Na, R. C. Hayward, Angew. Chem. Int. Ed. 2015, 54, 5434.
[10] L. Montero de Espinosa, W. Meesorn, D. Moatsou, C. Weder, Chem. Rev. 2017, 117, 12851.
[11] F. Schmitt, O. Piccin, L. Barbé, B. Bayle, Front. Robot. AI 2018, 5, 84.
[12] E. Diller, J. Zhuang, G. Zhan Lum, M. R. Edwards, M. Sitti, Appl. Phys. Lett. 2014, 104, 174101.
[13] H. Lang, M. Totaro, L. Beccai, Adv. Sci. 2018, 5, 1800541.
[14] H. Choi, J. Choi, S. Jeong, C. Yu, J. Park, Smart Mater. Struct. 2009, 18, 115017.
[15] J. Hu, X. Li, Y. Ni, S. Ma, H. Yu, J. Mater. Chem. C 2018, 6, 10815.
[16] F. Mugele, J. C. Baret, J. Phys.: Condens. Matter 2005, 17, R705.
[17] L. F. Cheow, L. Yobas, D. L. Kwong, Appl. Phys. Lett. 2017, 90, 054107.
[18] S. X. Cho, H. J. Moon, C. J. Kim, J. Microelectromech. Syst. 2003, 12, 70.
[19] V. Srinivasan, V. K. Pamula, R. B. Fair, Lab on a Chip 2004, 4, 310.
[20] A. W. Martinez, S. T. Phillips, E. Carrilho, S. W. Thomas, H. Sindi, G. M. Whitesides, Anal. Chem. 2008, 80, 3699.
[21] T. B. Jones, Langmuir 2002, 18, 4437.
[22] Q. Ho Quang, T. Thai Doan, T. Doan Quoc, L. Ly Nguyen, T. Nguyen Manh, Opt. Quant. Electron. 2020, 52, 189.
[23] A. García-Cabañas, A. Blázquez-Castro, L. Arizmendi, F. Aguilló-López, M. Carrascosa, Crystals 2018, 8, 65.
[24] C. Lipin, L. Shaobei, F. Bolin, Y. Wenbo, W. Donghui, S. Lihong, C. Hongjian, B. Dechao, S. Shihao, Sci. Rep. 2016, 6, 29166.
[25] F. Li, X. Zhang, K. Gao, L. Shi, Z. Zan, G. Liang, E. R. Mugisha, H. Chen, W. Yan, Opt. Exp. 2019, 27, 25767.
[26] X. Zhang, K. Gao, Z. Gao, Z. Shi, X. Liu, M. Wang, H. Chen, W. Yan, Opt. Lett. 2020, 45, 1180.
[27] E. Muñoz-Cortés, A. Puerto, A. Blázquez-Castro, L. Arizmendi, J. L. Bella, C. López-Fernández, M. Carrascosa, A. García-Cabañas, Opt. Lett. 2020, 45, 1164.
[28] A. D. Wexler, M. López Sáenz, O. Schreer, J. Woiwetschläger, E. C. Fuchs, J. Vis. Exp. 2014, 91, e51819.
[29] J.-T. Wu, M. S. Carvalho, S. Kumar, J. Non-Newton. Fluid Mech. 2019, 274, 104173.
[30] A. H. Paulitsch-Fuchs, A. Zsohára, A. D. Wexler, A. Zauner, C. Kittinger, J. Valença, E. C. Fuchs, Biochem. Biophys. Rep. 2017, 10, 287.
[31] S. Coppola, V. Vesgini, G. Nasti, O. Gennari, S. Grilli, M. Ventre, M. Iannone, P. A. Netti, P. Ferraro, Chem. Mater. 2014, 26, 3357.
[32] S. Coppola, G. Nasti, M. Todino, F. Olivieri, V. Vesgini, P. Ferraro, ACS Appl. Mater. Interfaces 2017, 9, 16488.
[33] I. A. Grimaldi, S. Coppola, F. Loffredo, F. Villani, G. Nenna, C. Minarini, V. Vesgini, L. Miccio, S. Grilli, P. Ferraro, Appl. Opt. 2013, 52, 7699.
[34] C. Granata, A. Vettoliere, M. Russo, Rev. Sci. Instrum. 2011, 82, 033901.
[35] P. Ferraro, S. Coppola, S. Grilli, M. Paturzo, V. Vesgini, Nat. Nanotechnol. 2010, 5, 429.
[36] S. Coppola, G. Nasti, B. Mandracchia, V. Vesgini, S. Grilli, V. Pagliarulo, P. Pareo, M. Manca, L. Carboni, G. Gigili, P. Ferraro, IEEE J. Sel. Top. Quantum Electron. 2015, 22, 1.
[37] S. Grilli, S. Coppola, G. Nasti, V. Vesgini, G. Gentile, V. Ambrogi, C. Farfagna, P. Ferraroa, RSC Adv. 2014, 4, 2851.
[38] G. Nasti, S. Coppola, F. Olivieri, V. Vesgini, V. Pagliarulo, P. Ferraro, Langmuir 2018, 34, 2198.
[39] S. Coppola, V. Vesgini, F. Olivieri, G. Nasti, M. Todino, B. Mandracchia, V. Pagliarulo, P. Ferraro, Appl. Surf. Sci. 2017, 399, 160.
[40] T. B. Jones, J. Electrost. 2001, 51–52, 290, https://doi.org/10.1016/S0304-3886(01)00074-2.